THE IN-PLACE POLLUTANTS PROGRAM

VOLUME VI

CONTAMINANT MOVEMENT FROM SEDIMENTS TO BIOTA

FEBRUARY 1991

Ontario
Environment
Environnement

ISBN 0-7729-7524-8

THE IN-PLACE POLLUTANTS PROGRAM

VOLUME VI

COMTAMINANT MOVEMENT FROM SEDIMENTS TO BIOTA

Report prepared for:

Water Resources Branch
Ontario Ministry of the Environment

FEBRUARY 1991

Cette publication technique
n'est disponible qu'en anglais

Copyright: Queen's Printer for Ontario, 1991
This publication may be reproduced for non-commercial purposes
with appropriate attribution

log 87-2330-037
PIBS 1426

THE IN-PLACE POLLUTANTS PROGRAM

VOLUME VI

CONTAMINANT MOVEMENT FROM SEDIMENTS TO BIOTA

Report prepared by:

D.R. Hart and D. Andrews
Beak Consultants Limited
14 Abacus Road
Brampton, Ontario
L6T 5B7

92-01661/

ACKNOWLEDGEMENT

Financial assistance and technical advice were provided by Environment Canada through the Polluted Sediment Committee of the Canada-Ontario Agreement. These contributions are gratefully acknowledged.

TABLE OF CONTENTS

		Page
1.0	INTRODUCTION	1.1
2.0	STUDY OBJECTIVES	2.1
3.0	METHODOLOGY	3.1
	3.1 General Approach	3.1
	3.2 Statistical Methods	3.2
4.0	RESULTS AND DICUSSION	4.1
	4.1 Review of Sediment Geochemistry	4.1
	4.2 Metal Residue Relationships	4.4
	4.2.1 Bottom Water and Bulk Sediments	4.4
	4.2.2 Sediment Fractions	4.5
	4.2.3 Complex Models	4.5
	4.2.4 Gut Correction	4.8
	4.2.5 Dry Weight Residues	4.10
	4.2.6 Taxonomic Effects	4.12
	4.2.7 Fish Age Effects	4.14
	4.2.8 Food Chain Effects	4.15
	4.3 Organic Residue Relationships	4.15
	4.3.1 Bottom Water and Bulk Sediments	4.15
	4.3.2 Gut Correction	4.18
	4.3.3 Dry Weight Residues	4.19
	4.3.4 Taxonomic Effects	4.19
	4.3.5 Fish Age Effects	4.21
	4.3.6 Food Chain Effects	4.22
5.0	CONCLUSIONS	5.1
6.0	RECOMMENDATIONS	6.1
7.0	REFERENCES	7.1

LIST OF TABLES

Table No.	
1.1:	Contaminants Measured in In-place Pollutants Program
1.2:	Study Locations and Number of Areas Sampled in In-place Pollutants Program
4.1:	Spearman Correlation of Metals in Fish with Bottom Water and Bulk Sediment Concentrations
4.2:	Spearman Correlation of Metals in Benthos with Bottom Water and Bulk Sediment Concentrations
4.3:	Spearman Correlation of Metals in Fish and Benthos with Concentration in F4 Sediment Fraction
4.4:	Shea and Tessier Models as Predictors of Heavy Metals in Fish
4.5:	Shea and Tessier Models as Predictors of Heavy Metals in Benthos
4.6:	Spearman Correlation of Ash-Corrected Metals in Benthos with Concentrations in Bottom Water and F4 Sediment Fractions
4.7:	Spearman Correlation of Chlorophenols and Chloroaromatics in Fish with Bottom Water and Bulk Sediment Concentrations
4.8:	Spearman Correlation of Chlorophenols and Chloroaromatics in Benthos with Bottom Water and Bulk Sediment Concentrations
4.9:	Spearman Correlation of PCB and Pesticides in Fish with Bottom Water and Bulk Sediment Concentrations
4.10:	Spearman Correlation of PCB and Pesticides in Benthos with Bottom Water and Bulk Sediment Concentrations
4.11:	Spearman Correlation of Polyaromatic Hydrocarbons in Fish and Benthos with Bulk Sediment Concentrations
4.12:	Significant Age Relationships of Lipid Normalized Organic Residues in Sculphins (Cottus bairdi)
4.13:	Significant Food Chain Relationships of Lipid Normalized Organic Residues in Sculpins (Cottus bairdi)

LIST OF FIGURES

Figure No.	
4.1:	Fish Metal Residues vs. Iron-Normalized F4 Sediment (Plot by species code)
4.2:	Fish Copper Residue vs. Shea Model Prediction
4.3:	Fish Metal Residues vs. Iron Normalized F4 Sediment (Plot by age code)
4.4:	Chlorophenol Residues vs. Bottom Water
4.5:	Benthos PAH Residues (Lipid-Normalized) vs. Bulk Sediment (TOC-Normalized)
4.6:	Age Effects on Fish Organic Residue Relationships

1.0 INTRODUCTION

The focus of public concern for aquatic environmental quality, and of corresponding environmental regulatory initiatives, has been shifting over the past decade from eutrophication issues towards effects of persistent toxic substances on ecosystem health (IJC, 1985, 1987). The Ontario Ministry of the Environment (MOE) In-place Pollutants Program was initiated in 1983 to evaluate the significance of persistent toxic substances in sediments and develop management strategies for ecosystem protection from sediment contamination. The program is supported in part by Environment Canada under terms of the Canada-Ontario Agreement (COA) on Great Lakes Water Quality.

Field studies carried out from 1983-1987 (Lomas and Persaud, 1987; Persaud and Lomas, 1987; Persaud et al., 1987, 1989; Jaagumagi et al., 1989) have generated a large quantity of data on contaminant concentrations in bulk sediments, various sediment fractions including interstitial water, bottom water, benthic biota, and bottom-feeding fish. These data are useful in addressing the movement of contaminants from sediments to biota. In addition, these studies have generated a large quantity of benthic enumeration data which are useful in determining benthic community impacts and in selection of appropriate indicator species for biomonitoring of sediment contamination. The chemical contaminants which have been determined in water, sediments and biota include PCBs, organochlorine pesticides, polyaromatic hydrocarbons (PAHs), chlorinated aromatics, chlorophenols and heavy metals (Table 1.1). The twenty study locations and the number of sampling sites at each location in each year are listed in Table 1.2.

Beak Consultants Limited (BEAK) was assigned the task of collating these data, and evaluating the nature of relationships (if any) between contaminant levels found in the sediments, and contaminant residues in benthic biota and bottom-feeding fish. In addition, recommendations were requested by the MOE on data manipulations and design of future monitoring activities to permit development of stronger residue relationships.

TABLE 1.1: CONTAMINANTS MEASURED IN IN-PLACE POLLUTANTS PROGRAM[1,2]

PCB/ Organochlorine Pesticides:	Aldrin, A-BHC, G-BHC, A-chlordane, G-chlordane, dieldrin, DMDT, endosulfan-I, endosulfan-II, endrin, endosulfan sulphate, heptachlor epoxide, heptachlor, mirex, oxychlordane, o,p-DDT, PCBs, p,p-DDD, p,p-DDE, p,p-DDT, HCB, OCS, hexachloroethane, HCBD
PAHs:	Phenanthrene, anthracene, fluoranthene, fluorene, pyrene, benzo(a)anthracene, chrysene, benzo(e)pyrene, benzofluoranthene, perylene, benzo(a)pyrene, benzo(g,h,i)perylene, dibenz(a,h)anthracene, ideno(1,2,3-cd)pyrene, benzo(b)chrysene, anthanthrene, coronene, dimethylbenz(a)anthracene, dioanthracene, naphthalene, acenaphthene, acenaphthylene
Chlorinated Aromatics:	Trichlorobenzene-(1,3,5), (1,2,4), (1,2,3) Trichlorotoluene-(2,4,5),(2,3,6), (2,6a) Tetrachlorobenzene-(1,2,3,5), (1,2,4,5), (1,2,3,4) Pentachlorobenzene
Chlorophenols:	Trichlorophenols-(2,3,4), (2,4,5), (2,4,6) Tetrachlorophenols-(2,3,4,5), (2,3,5,6) Pentachlorophenol
Metals:	Zn, Cu, Pb, Fe, Mn, As, Cr, Hg, Cd

1 1983-85 analyses primarily for metals and PCB/OCs; 1986-87 analyses include all contaminant groups.

2 Sediment characterization also includes total organic carbon (TOC), oil and grease, and grain size; tissue characterization also includes lipid content.

TABLE 1.2: STUDY LOCATIONS AND NUMBER OF AREAS SAMPLED IN IN-PLACE POLLUTANTS PROGRAM

Location	1983[1]	1984[1]	1985A[2,3]	1985B[2]	1986[2]	1987[2]
Toronto Harbour and Waterfront	42		20	27		12
Hamilton Harbour	10					
Frenchmans Bay	5					
Oakville Harbour				9		
St. Catharines				6		
Penetang Harbour				10		
Midland Bay				10		
Bay of Quinte				10		
Wheatley Harbour			3			
Detroit River		8		10		
Niagara River				8		
St. Clair River	8	8		10	9	
St. Marys River	8		5	10		7
Kam River					9	
St. Lawrence River:						
o Kingston						
o Maitland		4				
o Cornwall					10	
Collingwood Harbour					19	
Grand River & Canagagigue Creek						9
Rice Lake and Otonabee River						14

[1] 1983-84 data only include bulk sediment chemistry, metals in geochemical fractions and invertebrate tissue levels.

[2] 1985-87 data also include bottom water chemistry, sculpin tissue levels and benthic enumeration.

[3] 1985A excludes benthic enumeration data.

2.0 STUDY OBJECTIVES

It was the purpose of the study to address a number of ancillary questions which are related to the central issue of relationships between sediment contaminants and contaminant residues in biota. In particular:

- o do the data need to be transformed to allow application of statistical evaluation techniques?
- o should the data be expressed on a wet weight or dry weight basis?
- o should the benthic data be gut-corrected or not?
- o should the biota residue data be lipid-corrected or not?
- o for the metals, what is the relationship between the different geochemical fractions in the sediment and the residue levels in biota?
- o what role do total organic carbon, oil and grease or other sediment chemical factors play in modifying contaminant uptake by biota from the sediments?
- o what is the role of water chemistry and physical factors in modifying contaminant uptake from the sediments?
- o what is the relation between levels of contaminants in benthos and in bottom-feeding fish? and
- o what are the species-to-species differences and similarities in contaminant residues and what type of benthic biota is the best indicator of contaminant levels in sediments.

BEAK examined each of these questions, with respect to each pertinent chemical parameter, by direct evaluation of relationships in the In-place Pollutants database, as well as by examination of approaches taken by other investigators.

3.0 METHODOLOGY

3.1 General Approach

The primary criterion for evaluation of each of the procedural questions listed in Section 2.0 was the ability of the procedure to elucidate relationships between sediment and biota contaminant levels. As part of this primary consideration, considerations of statistical validity and bioaccumulation theory are also relevant. In other words, valid relationships can only be demonstrated by statistically valid methods, and relationships to be tested must be consistent with current evidence of bioaccumulation mechanisms.

The bioaccumulation literature was reviewed to establish the plausibility of relationships to be tested, and to provide a defensible rationale for each model. In addition, we considered approaches of other investigators to modelling contaminant bioavailability, correcting residues for gut contents, and use of wet or dry-weight contaminant data. The key technical tasks performed following the literature review included:

- document review and model development;
- In-place Pollutants data manipulation and QA checks; and
- statistical model evaluation.

The models tested involved either bulk sediment contaminant concentrations, or concentrations of metals in different geochemical sediment fractions, or contaminant concentrations in bottom waters, as predictors of tissue residues. Predictor variables can be normalized by concentrations of sediment constituents that adsorb or complex toxic contaminants (e.g., total organic carbon (TOC), iron oxides, manganese oxides). Tissue residues can be normalized by tissue lipid content, since non-polar organics are held primarily in the lipid pool. Various combinations of predictor variables and normalizing factors were used in model construction.

The In-place Pollutants database does not contain an exact equivalent of iron oxide or manganese oxide. However, roughly equivalent estimates of iron and manganese oxide were derived from the iron and manganese contents, respectively, of the reducible (F2 + F4) geochemical fraction.

These estimates were variously used to normalize sediment fraction or bulk sediment predictors in evaluation of Tessier et al. (1984), Shea (1988) and other metal bioavailability models. Models are described in more detail with the results in Section 4.0.

The In-place Pollutants Program extracts metals bound to iron and manganese oxides in two fractions, an easily reducible fraction (F2) and a moderately reducible fraction (F4). Both acid extractions capture metals from iron and manganese oxides, although the latter extraction is considerably more rigorous and more specific to iron-oxide bound metals. The sum of iron in F2 + F4 is the closest approximation to total iron-oxide possible using the In-place Pollutants fractionation scheme.

3.2 Statistical Methods

Simple residue relationships involving single predictor variables were evaluated non-parametrically by calculation of Spearman rank correlation coefficients. However, more complex models involving multiple predictors were evaluated parametrically by multiple regression analysis. The parametric procedures are typically more powerful, but are based on assumptions (e.g., normality of residuals) that cannot always be achieved.

The single most important factor influencing normality in the In-place Pollutants data, particularly for organic chemical parameters, is the prevalence of concentrations in sediment, water or biota which fall below the Limit of Detection (LOD). It is now generally recognized that the best method of reporting data above an instrument threshold (W, if one exists) and below the LOD is as a quantitative concentration with

a T flag (EPA, 1980; ASTM, 1985; Hunt and Wilson, 1986; Gilbert, 1987). The MOE is now implementing such a reporting system; however, older data, particularly for organics, have been reported as ND at concentrations below the LOD. Both T and W data were included in the statistical analysis at their face values. ND data were included at the value of the detection limit.

Trace data (T flagged) should always be used in mean or variance estimation and in estimation of correlation or regression parameters. Special methods of mean and variance estimation are recommended for inclusion of censored samples (W or ND data) in statistical summaries (Cohen, 1961; Helsel, 1986; Gilbert, 1987). However, methods for estimation of correlation and regression statistics with censored data are not available.

Benthic invertebrate and bottom-dwelling fish data sets were treated separately in model development and testing. Differences in residue relationships among taxa within data sets were explored by plotting with taxonomic codes as plotting symbols. Similarly, differences in residue relationships among age classes of sculpin species were explored by plotting with age-class codes as plotting symbols. In addition, the dependence of lipid content on fish age class was evaluated by regression analysis.

Residue and lipid data were expressed on a wet weight basis, and sediment data on a dry weight basis, for all statistical analysis of 1983-87 data. Wet/dry weight conversion factors were recorded by taxon at each location in 1987, and correlations were compared with and without conversion in this smaller data set.

All statistical evaluations were performed on IBM XT/AT computers using standard statistical procedures (Steel and Torrie, 1960; Sokal and Rohlf, 1981) as implemented in SPSS/PC+ (Norusis, 1986) and SAS (Saffer, 1987) software packages.

4.0 RESULTS AND DISCUSSION

4.1 Review of Sediment Geochemistry

Availability of trace metals to benthic deposit-feeders is intimately dependent upon the physical-chemical forms in which the metals are present in the sediments (Luoma and Jenne, 1976a,b; Bryan and Hummerstone, 1977; Bryan and Uysal, 1978; Luoma and Bryan, 1978, Luoma, 1983; Tessier et al., 1984). The accumulation of trace metals by benthic organisms is only poorly predicted from total concentrations in the sediments (Bryan and Hummerstone, 1977; Bryan 1985; Neff et al., 1978; Marquenie et al., 1983). In many studies, attempts have been made to correlate the heavy metal contents of deposit-feeding macrofauna with particular chemical fractions of the metal in the sediments. These chemical fractions represent selective or sequential extractions of sediment-bound metals by various extraction techniques (Gibbs, 1973; Guptu and Chen, 1975; Tessier et al., 1979, Forstner and Wittman, 1983). Some of these are listed in Table 4.0. Sequential or selective extraction procedures have also been applied to sediments in studies reported by Calmano and Forstner, 1983; Forstner, 1982; Reuther et al., 1981; Rapin et al., 1983; Evans et al., 1988; and Andrews, 1988, 1989.

The metal extraction procedure adopted by the In-Place Pollutants program divides sediment bound metals into six fractions including interstitial (IW), cation exchangeable (F1), easily reducible (F2), organic or sulphide bound (F3), moderately reducible (F4) and residual (F5). Cation exchangeable metals are weakly (electrostatically) adsorbed to sediment particles (e.g., clays) and considered in equilibrium with the interstitial phase. These metals are extracted by cation exchange with NH_4OAC. The easily reducible fraction represents metals attached by weak chemical bonds to solids (e.g., carbonates). These can be released under anaerobic conditions. They are extracted under mildly reducing/acidic conditions with hydroxylamine hydrochloride. The organic fraction represents metals associated with organic complexes after oxidative extraction with H_2O_2. The process also removes metals associated with sulphides (Tessier et al., 1979) which can be released under oxidizing conditions. The moderately reducible

fraction represents metals associated with iron and manganese oxides and is extracted under strongly reducing/acidic conditions. These metals are released under anaerobic conditions (Jackson et al., 1978). The residual fraction represents metals bound within crystal lattices of minerals and extracted with strongly oxidizing acids (HNO3 and $HClO_4$) at elevated temperatures. The first four fractions are considered to be available to benthic organisms under appropriate aerobic or anaerobic conditions.

The ultimate goal of bioavailability studies involving sequential or selective extractions of sediments is to find a fraction or combination of fractions to serve as a universal predictor of trace metal contents in benthic invertebrates. Thus, Luoma and Bryan (1978) related the lead content of the bivalve Scrobicularia in a British estuary to the Pb/Fe ratio in the sediments extracted with 0.1 N HCl. This weak acidic extract was supposed to resemble the gut environment. Luoma and Jenne (1976a,b) labelled natural and artificial sediments with heavy metal radioisotopes and found good correlations between uptake of zinc-65 and cadmium-109 in the deposit-feeder Macoma balthica with readily-exchangeable zinc-65 and ethanol-extracted cadmium-109 respectively in the sediments. Uptake from organic detritus was very low. Luoma and Bryan (1979) related the zinc content of the bivalve Scrobicularia to easily-exchangeable zinc in the sediments. In the same study, the zinc content of the bivalve Macoma balthica from San Francisco Bay was related to the ratio of oxide-bound iron divided by easily exchangeable manganese and organic carbon in the sediments. Tessier et al. (1984) related the copper concentration in the bivalve Elliptio (actually a filter feeder) to the ratio of Cu (exchangeable + carbonate-bound + Fe/Mn oxide-bound) to iron oxide in freshwater sediments. A more complete list of extractions used in metal residue prediction is presented in Table 4.0.

In many of the studies listed above and in Table 4.0, significant correlations were frequently complex and involved multiple fractions and ratios of fractions. The relationships were often improved by normalizing metal concentrations in the fractions with respect to iron or amorphous iron (Campbell et al., 1988; Tessier et al., 1982, 1984; Luoma and Bryan, 1978). This suggests that iron controls bioavailability by either

competing directly with trace metals in the gut for binding sites or, as amorphous iron oxides, by binding with metals in the sediments and reducing their bioavailability.

The interstitial, exchangeable and reducible fractions recur as potential sources of sediment-bound metals, whereas organics and Fe-Mn oxides recur as scavengers that release under certain conditions (Campbell et al., 1988). The high availability of interstitial metals is suggested in studies by Dean (1974) who found that tubificids accumulated zinc-65 directly from water but not from labelled sediments, and Prosi (1981) who concluded that Tubifex absorbed interstitial cadmium rather than particle-bound cadmium from Rhine River sediments. Andrews (1988) found in laboratory studies that tubificids absorbed three orders of magnitude more zinc-65 from water solutions than from sediments of the same activity. An autoradiographic study with lead-210 also suggested that soluble lead is more available than sediment-bound lead (Andrews 1988; 1989). Lead-210 from both sources was found in the same tissues of the worms, indicating that the metal is metabolized similarly regardless of the source of the metal or mode of entry into the organism.

Recently, the use of sediment chemical fractions to predict animal burdens of metals has come under more critical scrutiny. Metal partitioning, especially of anoxic sediments can change on storage or introduction of oxygen (Thomson et al., 1980; Campbell and Tessier, 1984; Rapin et al., 1986). Ideally, anoxic sediment should be extracted immediately under nitrogen. Only freezing or a very short period of wet storage at 4 C is recommended (Thomson et al., 1980). Sediments should only be dried for total sediment concentrations of non-volatile metals. Many of the early studies did not follow these precautions.

In addition, tests of the selective extraction procedure itself have indicated that redistribution of the metals between the phases occurs during the extraction procedure. Kheborian and Bauer (1987) doped specific trace metals into the various chemical phases of an artificial sediment which was then subjected to the sequential extraction procedure of Tessier et al. (1979). These authors found that the trace metals were not

recovered in the appropriate fractions. Their results raise serious questions regarding the use of selective extraction procedures, even when these are operationally defined and used only for comparative purposes.

By sampling and extracting only surface sediments, most studies have also neglected the vertical distribution of sediment chemical fractions in relation to animal feeding behaviour. Andrews et al. (1985) showed that the easily exchangeable fraction of cobalt in Ottawa River sediments decreased from 12% of the total cobalt concentration at the surface to less than 1% at 3.5 cm depth. An organism, such as a tubificid, feeding at 2-3 cm in the sediments and defecating at the surface would be exposed to far less of this fraction than suggested from a surface sample. Similar gradients in the chemical fractionation of zinc were observed by Andrews (1988) and have been noted by other authors (Reuther et al., 1981; Calmano and Forstner, 1983; Rapin et al., 1983; and Forstner, 1982).

4.2 Metal Residue Relationships

4.2.1 Bottom Water and Bulk Sediments

Metal residues in fish (Table 4.1) and benthos (Table 4.2) are poorly correlated with concentrations in bottom water and bulk sediment prior to normalization. Normalization of the wet-weight residues by iron oxide estimates, manganese oxide estimates, or measured TOC, tends to improve the correlation, particularly for fish. Sediments normalized by TOC provide the best general predictor of biotic residues from bulk sediment/water information, both for fish and benthos. Nevertheless, the relationships are not strong. Zinc is the most predictable metal, both for fish and benthos, with normalized sediment correlations of 0.74 and 0.79, respectively.

The estimates of iron oxide and manganese oxide are only approximate. Moreover, they pertain to the fine (less than 63 u) sediment fraction since only the fines were subjected to geochemical partitioning. Direct bulk sediment measurements of iron and

manganese oxides might provide a superior normalizing factor for bulk sediments as residue predictors.

4.2.2 Sediment Fractions

Metal concentrations in individual sediment fractions (F1, F2, F3, F4), interstitial water (IW), and combinations of these fractions were evaluated for relationships with metal residues in biota. Combinations considered included:

- sum of IW plus F1 through F4, and
- sum of F1 plus F2 plus F4.

Each potential residue predictor was evaluated with and without normalization by the iron oxide estimate, manganese oxide estimate and measured TOC. Only the F4 fraction was better related than bulk sediment to metal residues in biota (Table 4.3). The best correlations were for fish, and the iron oxide estimate was generally the best normalizing factor for F4 as a residue predictor.

Figure 4.1 illustrates some of the best fish residue - F4 fraction relationships (Spearman correlations from 0.73 to 0.86). Relationships for these metals (copper, arsenic, manganese, iron, zinc) are approximately linear. For manganese, there is some evidence of a dichotomous relationship, with rednose dace (species 5) and white sucker (species 8) following a steeper residue relationship than other fish species.

4.2.3 Complex Models

Two models of heavy metal bioavailability from the literature (Tessier et al., 1984; Shea, 1988) were evaluated by regression analysis. The Tessier model is empirically derived from field correlations. It was approximated by:

$$C_b = a + k \left[\frac{F1 + F2 + F4}{FeOx} \right]$$

where: F1, F2 and F4 = metal concentrations in sediment fraction,
FeOx = iron concentration in fractions F2 + F4,
C_b = metal residue in biota,
k = slope, and
a = an intercept.

Tessier et al. (1979) assumed an intercept of zero; however, we permitted an intercept as a model calibration factor and tested whether it was significantly non-zero.

In the original Tessier model (Tessier et al., 1984), the numerator consisted of the sum of the easily exchangeable, carbonite-bound and Fe/Mn oxide bound metal fractions. This quantity was approximated in our regression by the sum F1 + F2 + F4. This approximation is probably quite accurate since carbonate-bound metals in the original model are extracted under the acidic conditions of extraction F2 (pH = 2.0). The denominator in the Tessier model is the total amount of iron oxide in the sediments. In our regression, this was approximated by the F2 + F4 sum, since both fractions contain the iron oxide bound metals.

The Shea (1988) model is essentially equivalent to that of DiToro et al. (1987). Both models are derived from equilibrium-partitioning principles, and assume that available metals are regulated by three independent absorption equilibrium with manganese oxides, iron oxides and organic carbon. The models are identical except that Shea's model refers to a reactive, metal absorbing organic fraction of the sediments while DiToro's model incorporates the total organic carbon as the metal absorbing fraction. The Shea and DiToro models were tested as a multiple and regression equation of the following form:

$$C_b = \frac{C_s}{a + k_1 MnOx + k_2 FeOx + k_3 TOC}$$

where: C_s = metal concentration in bulk sediment,
MnOx = manganese concentration in fractions F2 + F4,
FeOx = iron concentration in fractions F2 + F4,
TOC = total organic carbon in bulk sediment,
k_1, k_2, k_3 = regression coefficients, and
a = an intercept.

Again, as with the Tessier model, concentrations of the adsorbing phases were approximated by the most appropriate In-place Pollutant fractions. Ideally, the three terms in the denominator should be expressed as concentrations on a bulk sediment basis. However, we were unable to estimate bulk oxide concentrations from the In-place Pollutants data. Shea (1988) assumed an intercept of zero; however, we permitted an intercept as a model calibration factor and tested whether it was significantly non-zero.

Table 4.4 shows the model coefficients, and overall model correlation with metal residues in fish. Table 4.5 provides similar data for model prediction of metal residues in benthos. The Shea model successfully predicted residues of copper, arsenic, cadmium, lead and zinc in fish; and chromium, arsenic, iron, cadmium and lead in benthos. The Tessier model successfully predicted residues of chromium, manganese and nickel, in fish only. However, model performance in general was inferior to that of the simple FeOx-normalized F4 fraction (Table 4.3). An example of the Shea model prediction for copper residues in fish is provided in Figure 4.2.

It is possible to theoretically derive Shea model coefficients from adsorption-desorption data, although these data are scarce in the literature. The coefficients are related to

the slope of the adsorption isotherms for each metal on each of the three adsorbing phases. The approach assumes that the adsorbing phases in the adsorption experiments are identical to those in natural sediments. Careful attention must also be paid to consistency of the units involved.

Coefficients derived in this manner for copper and cadmium, along with the data sources, are listed below:

Metal	k_1	k_2	k_3 (L/g)	Source
Copper	7,339	205	336	Oakley et al. (1981)
Cadmium	15	4.4	0.2	Oakley et al. (1981)
Cadmium	1,500	130	17	Davis-Colley et al. (1984)

The cadmium models did not achieve significant prediction of cadmium residues in either fish or benthos. The copper model was significant for fish, but inferior to the model that was statistically derived from In-place Pollutants data (Figure 4.2).

4.2.4 Gut Correction

Studies on aquatic consumers indicate that gut contents contribute significantly to the body burden of metals. Elwood et al. (1976) found a mean difference of 57 $\pm$ 8% in a whole range of metal concentrations in Tipula sp. before and after gut evacuation. Andrews (1988), in a study of zinc bioavailability to tubificids, found that isolating the worms in groups of three or fewer and removing the feces permitted effective evacuation of the gut by eliminating coprophagy. This process, however, is time-consuming and may not be feasible in a major benthic survey.

Using the technique of Bindra and Hall (1977), Chapman (1985) estimated the sediment metal contents in the guts of tubificids to vary from 16.4% of the total body content for zinc to 39.7% for nickel. Larger percentages were determined in ammocoete and chironomid larvae (see also Chapman et al., 1980). Gut sediment

metal contents were calculated by collecting the undigested residue from a peroxide/nitric acid digest of the organism and assuming this residue to represent sediments in the gut of known metal concentration. Chapman concludes that metal analyses of whole benthic animals must include a gut sediment correction. In a similar correction, the ash content of the organism is assumed to represent the sediment content in the gut, and the body burden is corrected accordingly (Persaud et al., 1987).

A gut correction based on ash content may not be relevant with organic contaminants or in fish. Using the ashing technique, Oliver (1987) found that sediments in the guts of tubificid worms comprised a negligible amount of the total organic contaminant concentration. These contaminants included 37 hydrocarbons, including PCBs. High ash contents in the skeleton of fish may result in an overestimate of the sediment content of the gut.

With In-place Pollutants data, we performed an ash-correction of metal residues in benthos for the purpose of comparing tissue/sediment correlations obtained with and without correction. The correction formula was as follows (Persaud et al., 1987):

$$C_b. = \frac{C_b - (C_s \cdot k_{ash})}{1 - k_{ash}}$$

where: $C_b.$ = corrected metal residue,
C_b = uncorrected metal residue,
C_s = metal concentration in dry sediment, and
k_{ash} = mass fraction of organism that is ash.

Corrections obtained with ash-corrected data are summarized in Table 4.6. These may be compared with correlations based on uncorrected benthic residue data in Table 4.2 (bottom water) and Table 4.3 (F4 sediment fraction). Very slight improvement is evident for copper and cadmium benthos/sediment correlations, while correlations are

slightly reduced for arsenic, nickel and lead. In general, correlations are poor and there is little, if any, advantage gained by ash-correction.

4.2.5 Dry Weight Residues

Although of considerable importance, the question of expressing tissue concentrations on a wet weight or dry weight basis is rarely addressed. Determination of wet weight concentrations in individual samples requires the removal of external water (usually with absorbant paper) and immediate weighing before the loss of internal water (Regvoi and Yalynskaya, 1960). This point is difficult to gauge accurately, and considerable variability in the measurements can arise even with standardization of the process (Winberg, 1971). An error in the weight measurement will result in a proportional error in the final concentration of a contaminant in an organism. Predictive correlations can, therefore, be obscured.

Trace metal concentrations are most often expressed on a dry-weight basis, preferably drying prior to analysis, or sometimes measuring moisture content on each sample to adjust the wet weight determination. A cursory examination of ten papers reporting metal contents in invertebrates indicates that concentrations in all of them were expressed by dry-weight (Bryan and Hummerstone, 1977, 1978; Bryan and Uysal, 1978; Bryan, 1979; Chapman et al., 1980; Crecelius et al., 1980; Krantzberg and Stokes, 1985; Luoma et al., 1985; Marquenie, 1985). In contrast, organic contaminants and volatile metals are often measured and expressed on a wet-weight basis because of potential losses of these contaminants during the drying process (e.g., Bryan, 1979; Oliver, 1987). Since most other studies in the literature (at least on metals) use dry weight units, it may be advantageous to express metal concentrations on a dry weight basis for purposes of comparison only.

Both metal and organic contaminants in the benthic fauna in the In-place Pollutants database have been determined on wet-weight samples, and are then corrected to dry weight with a taxon-specific conversion factor (Persaud et al., 1987). The application

of a common correction factor to all the measurements of body burden offers no direct advantage in the search for predictive relationships within the benthic database. However, if different correction factors are used for different taxa in a mixed-species database, the correction will eliminate error associated with taxonomic variation in moisture content, and could make general tissue-sediment relationships easier to detect. Thus, the potential usefulness of moisture correction by taxon depends on the taxonomic mix of the data set to be evaluated for residue relationships.

The benthic data set consists primarily of oligochaetes, while the fish data set consists primarily of sculpins. With so little taxonomic variation in the data, it is unlikely that application of taxon-specific dry/wet weight conversion factors would appreciably alter the residue relationships obtained. Moreover, since taxonomic differences in residue relationships are usually not evident within the benthic or fish data sets (Section 4.2.6), there is little room for improvement by application of taxon-specific dry/wet conversions.

The dry/wet weight ratios for various taxa, based on 1986-87 surveys, and on other published literature, are summarized below:

Taxon	Average Ratio	Standard Deviation	Source
Oligochaeta (lumbriculid)	0.20	0.02	Survey data (1986-87)
Chironomidae	0.11	0.03	Survey data (1986-87)
Amphipoda (Gammarus)	0.15	0.02	Survey data (1986-87)
Odonata	0.16	-	Survey data (1986-87)
Ephemeroptera (Hexagenia)	0.16	0.04	Survey data (1986-87)
Decapoda (shrimp)	0.16	-	Survey data (1986-87)
Tricoptera	0.15	-	Survey data (1986-87)
Sculpins	0.27	0.04	Survey data (1986-87)
Amphipoda (Hyallela)	0.23	-	Borgmann et al. (1989)

Oligochaeta	0.15	-	Kasprzak (1984)
Sculpins	0.24	-	Bormann and Whittle (1983)

Ratios vary by as much as .03 to .08 between sources, for a given taxon, and similar variation between collections of a single taxon is likely in the In-place Pollutants data.

Parallel wet and dry analytical determinations, or moisture determinations on individual samples, would ideally be used to compare the utility of wet-weight vs. dry-weight data in elucidation of residue relationships. It could probably be shown that such dry weight data are less variable (even within taxa) and better related to sediment characteristics. However, data are not available to permit this evaluation.

4.2.6 Taxonomic Effects

The taxonomic dominance of the In-place Pollutants data by oligochaetes and sculpins is illustrated by the following taxonomic breakdown of the number (N) of paired (tissue-water, tissue-sediment) observations on copper:

Taxon	Species Code	N Tissue-Water	Approx. % of Total	N Tissue-Sediment	Approx. % of Total
Oligochaeta (lumbriculid)	2,3	42	54	119	74
Chironomidae	1	20	25	24	15
Amphipoda (Gammarus)	5,7	12	15	12	8
Neuroptera (Sialis)	6	1	1	1	1
Ephemeroptera (Hexagenia)	4	4	5	4	2
TOTAL BENTHOS		79	100	160	100

Taxon	Species Code	N Tissue-Water	Approx. % of Total	N Tissue-Sediment	Approx. % of Total
Cottus bairdi (sculpin)	1	62	61	60	58
Cottuscognatus (sculpin)	2	9	8	10	9
C.b.-C.c. (hybrid)	3,4	5	5	7	6
Cottus sp.	0	5	5	5	5
Rednose Dace	5	4	4	4	4
Longnose Dace	6	4	4	4	4
Dace	-	4	4	4	4
Emerald Shiner	7	4	4	4	4
White Sucker	8	5	5	5	5
Trout Perch	9	0	0	1	1
TOTAL FISH		102	100	104	100

Copper is the largest of the heavy metal data sets, and this distribution is representative of most other contaminants.

Examination of Figures 4.1 and 4.2 does not suggest any major taxonomic differences in metal residue relationships, within the benthos or fish data sets. There is considerable residual variation in all the relationships detected; however, this is not obviously attributable to species pooling. Sample sizes of taxa other than oligochaetes and sculpins are small, and therefore would permit very little resolution in characterization of other species-specific residue relationships.

There are minor differences between fish and benthos in the strength and type of metal residue relationships detected. However, in both groups, the residues tend to be better related to the sediments than to the bottom-water, and better related to the F4 sediment fraction than to the bulk sediment. The fish relationships tend to be stronger and detectable for more metal parameters.

4.2.7 Fish Age Effects

Only sculpins varied sufficiently in age to permit evaluation of age effects. Age effects on metal residues were statistically examined for Cottus bairdi the dominant sculpin in the database. Ages ranged from two to seven years, as illustrated by the following age breakdown of the number (N) of paired (tissue-water, tissue-sediment) observations on copper:

Age (years)	N Tissue-Water	Approx. % of Total	N Tissue-Sediment	Approx. % of Total
2	6	12	7	15
2-3	2	4	2	4
3	9	19	8	17
3-4	5	10	5	10
4	12	25	11	23
4-5	2	4	3	6
5	8	16	7	15
5-6	3	6	3	6
6	1	2	1	2
6-7	1	2	1	2
TOTAL	49	100	48	100

There is fairly even representation of different ages in the database. Distributions associated with other heavy metal contaminants are similar.

Correlation of C. bairdi metal residues with age did not indicate a significant positive age relationship for any metal except nickel (r = 0.26). Weak negative age relationships were observed for arsenic, manganese, aluminum, lead and iron (r = -.37,

-.40, -.26, -.31, -.34). Plots of residue relationships with water and sediment variables, using age as a plot symbol, did not suggest any partitioning of relationships according to age class. Examples of these plots are illustrated in Figure 4.3.

4.2.8 Food Chain Effects

Cottus bairdi is a generalized bottom feeder, known to consume oligochaetes, amphipods and most insect larvae or nymphs. Accordingly, food chain effects were examined by matching C. bairdi residues with each benthic tissue sample from the same time and place. No metals displayed significant positive fish-benthos correlations.

4.3 Organic Residue Relationships

4.3.1 Bottom Water and Bulk Sediments

Sediment chemical factors which may modify contaminant uptake by biota include TOC or components (POC, DOC, Hassett and Anderson, 1982; McCarthy and Black, 1986; Piemontesi and Baccini, 1986; Campbell and Evans, 1987; Landrum et al., 1987), solvent extractables (oil and grease), pH (Lewis and McIntosh, 1986; Rodgers, 1987) and oxygen regime (Sakata, 1985). It is generally recognized that TOC is the primary modifier of availability of non-polar organic contaminants to biota. Partitioning of such organic compounds is governed by chemical competition between the organic carbon pool in the sediment and the lipid pool of the organism. This relationship can be expressed mathematically as follows (MacFarland, 1984; Rubenstein and Lake, 1986):

$$\frac{C_o}{L_f} = B_{oc}\,\frac{C_s}{TOC_s}$$

-.40, -.26, -.31, -.34). Plots of residue relationships with water and sediment variables, using age as a plot symbol, did not suggest any partitioning of relationships according to age class. Examples of these plots are illustrated in Figure 4.3.

4.2.8 Food Chain Effects

Cottus bairdi is a generalized bottom feeder, known to consume oligochaetes, amphipods and most insect larvae or nymphs. Accordingly, food chain effects were examined by matching C. bairdi residues with each benthic tissue sample from the same time and place. No metals displayed significant positive fish-benthos correlations.

4.3 Organic Residue Relationships

4.3.1 Bottom Water and Bulk Sediments

Sediment chemical factors which may modify contaminant uptake by biota include TOC or components (POC, DOC, Hassett and Anderson, 1982; McCarthy and Black, 1986; Piemontesi and Baccini, 1986; Campbell and Evans, 1987; Landrum et al., 1987), solvent extractables (oil and grease), pH (Lewis and McIntosh, 1986; Rodgers, 1987) and oxygen regime (Sakata, 1985). It is generally recognized that TOC is the primary modifier of availability of non-polar organic contaminants to biota. Partitioning of such organic compounds is governed by chemical competition between the organic carbon pool in the sediment and the lipid pool of the organism. This relationship can be expressed mathematically as follows (MacFarland, 1984; Rubenstein and Lake, 1986):

$$\frac{C_b}{L_f} = B_{oc} \frac{C_s}{TOC_f}$$

where: C_b = concentration in whole organism,

L_f = lipid fraction of organism (0 to 1),

B_{oc} = sediment bioconcentration factor (organic carbon normalized),

C_s = concentration in whole sediment, and

TOC_f = total organic carbon fraction of sediment (0 to 1).

This model was tested in a preliminary evaluation In-place Pollutants data for PCB/OCs in preparation for derivation of MOE sediment quality guidelines (BEAK, 1987a). It was compared to more complex models which also involved solvent extractables and particle size (Nau-Ritter and Wuester, 1983). The complex models were not significantly superior to the TOC model, suggesting that TOC is the primary factor regulating availability of PCB/OCs to biota. In the present study, the concept of lipid and TOC normalization was re-evaluated, particularly with respect to PAHs, chloroaromatics and chlorophenols, which were not previously considered.

A large body of research on sediment normalization theory sponsored by the U.S. EPA has confirmed that TOC is the single most important factor governing bioavailability of non-polar organic contaminants (e.g., Pavlou and Weston, 1983, 1984; Bolton et al., 1985; Kadeg et al., 1986; Shea, 1988). Interim sediment quality guidelines developed for such compounds by the EPA Criteria and Standards Branch (Battelle, 1988) were expressed in TOC-normalized units (i.e., ug/g C). Similarly, draft guidelines developed by BEAK (1988) for the MOE were expressed in this manner. On the other hand, partitioning theory for polar organics is very poorly understood and cannot yet support a normalization model (Shea, 1988).

Chlorophenols and Chloroaromatics

Residues of chlorophenols and chloroaromatics in fish (Table 4.7) and benthos (Table 4.8) were not strongly correlated, in general, with concentrations in water and sediment.

Tetrachlorophenolic residues in both fish and benthos were correlated with water concentrations. This relationship was strongest in fish (r = 0.70 to 0.94), and also extended to some trichlorophenols (2,4,6) in fish. Neither lipid normalization of tissue nor TOC normalization of water were generally useful in residue prediction.

Benthic residues of 2,4,6-TCP were correlated with concentrations in sediment (r = 0.74), and again, normalization did not improve the relationship. Correlations involving chloroaromatics were rare and, when they occurred, always weak.

Figure 4.4 illustrates the tetrachlorophenolic residue relationships, plotted by age for fish, and by taxon for benthos. All the fish are C. bairdi. There is little evidence of taxonomic variation in the form of these relationships within the benthic database; however, the greatest residue accumulations in contaminated areas occur in oligochaetes (species 2).

PCB and Pesticides

Residues of PCB and organochlorine pesticides in fish (Table 4.9) and benthos (Table 4.10) were very poorly correlated with concentrations in water and sediment. Most of these compounds were rarely detected in water, and many were never detected. Their hydrophobic nature, and the associated difficulty of analytical detection in water, makes a water-biota relationship unlikely. However, the sediment-biota relationships were not much better. The highest rank correlations involved aldrin in benthos and water, without normalization (r = 0.59), and DMDT in fish and sediment, with normalization (r = 0.61).

Polyaromatic Hydrocarbons

Polyaromatic hydrocarbons (PAHs) are strongly hydrophobic and were not measured in water. Biota-sediment rank correlations are listed in Table 4.11 for both fish and benthos. Benthic residues, in general, were better correlated than fish residues with

PAH concentrations in sediment. Fluorene and anthracene are two exceptions, for which fish residue relationships were superior. Acenaphthene residues were not correlated with sediment concentrations in either fish or benthos.

Lipid normalization of tissues, or TOC normalization of sediments, or both, generally improved the sediment-biota relationship. The most widely applicable model would involve normalization of both tissue and sediment, as suggested previously by Rubenstein and Lake (1986).

Figure 4.5 illustrates some of the better benthos-sediment PAH relationships (r = 0.67 to 0.73), all based on normalization of both tissue and sediment. There is little evidence of taxonomic differences in benthos-sediment relationships within the benthic data set. However, the amphipods (Gammarus, species 9) typically have higher PAH residues (or lower lipid) than oligochaetes (species 2), and also reside in more contaminated (or lower TOC) sediments. This taxonomic difference contributes to the observed residue relationship. Relationships are clearly log normal for some PAHs such as acenaphthylene which vary over five orders of magnitude in sediments.

4.3.2 Gut Correction

Most examples of gut correction in the literature involve metal residues (Section 4.2.4). Application of gut correction to organic residues in tubificid oligochaetes has been shown to be unnecessary (Oliver, 1987). Accordingly, since oligochaetes dominate the In-place Pollutants benthic data, gut correction was not attempted for organics in benthos during the present study. Gut correction based on ash content of the organism was not considered appropriate for fish because of the high ash content of the fish skeleton.

4.3.3 Dry Weight Residues

The use of taxon-specific dry/wet weight conversion factors is discussed in Section 4.2.5. While there may be an advantage in drying prior to analysis for metals, and expressing results on a dry-weight basis for purposes of comparability to other data, organic contaminants are usually measured in fresh samples and expressed on a wet-weight basis because of potential contaminant losses during drying (Bryan, 1979; Oliver, 1987). Moreover, application of taxon-specific conversion factors can only serve to eliminate variability in mixed-species data sets due to moisture differences among taxa. Neither the survey data nor the published literature support consistent taxonomic differences in moisture and, since the fish and benthic data sets are respectively dominated by sculpins and oligochaetes, dry/wet conversion by taxon was felt to be unnecessary.

4.3.4 Taxonomic Effects

The taxonomic dominance of the In-place Pollutants data by oligochaetes and sculpins is illustrated by the following taxonomic breakdown of the number (N) of paired (tissue-water, tissue-sediment) observations on the pesticide benzene hexachloride (BHC):

Taxon	Species Code	N Tissue-Water	Approx. % of Total	N Tissue-Sediment	Approx. % of Total
Oligochaeta (lumbriculid)	2,3	52	50	86	61
Chironomidae	1	26	25	28	20
Amphipoda (Gammarus)	7,9	12	11	12	9
Odonata	6	2	2	2	1
Ephemeroptera (Hexagenia)	4	7	7	7	5
Hirudinea	5	4	4	4	3
Tricoptera	8	1	1	1	1
TOTAL BENTHOS		104	100	140	100

Cottus bairdi (sculpin)	1	60	73	74	70
Cottus cognatus (sculpin)	2	9	11	10	9
C.b.-C.c. (hybrid)	3,4	0	0	0	0
Cottus sp.	0	1	1	3	3
Rednose Dace	5	2	3	3	3
Longnose Dace	6	1	1	4	4
Dace	-	1	1	1	1
Emerald Shiner	7	1	1	1	1
White Sucker	8	4	5	5	5
Trout Perch	9	3	4	4	4
TOTAL FISH		82	100	105	100

BHC is one of the largest of the organic data sets, and this distribution is representative of most other contaminants.

Examination of Figures 4.4 and 4.5 does not suggest any taxonomic differences in organic residue relationships within the benthos or fish data sets. The amphipods tend to have higher PAH residues, and to reside in more contaminated (or lower TOC) sediments, than the oligochaetes. However, this is not inconsistent with a common tissue sediment relationship. There is considerable residual variation in all the organic relationships, but this is not obviously attributable to species pooling. Sample sizes of taxa other than oligochaetes and sculpins are small, and therefore would permit very little resolution in characterization of other species-specific relationships.

There are differences between fish and benthos in the strength and type of organic residue relationships detected. In both groups, the tetrachlorophenolic residues were primarily related to concentrations in water, without normalization, but this relationship was stronger in fish. Trichlorophenol (2,4,6) residue was primarily related to water concentration for fish, but sediment concentration for benthos. The polyaromatic

hydrocarbons (PAHs) were correlated with sediments for both fish and benthos, but the correlations were typically better for benthos.

4.3.5 Fish Age Effects

Since only sculpins exhibited appreciable age variation, and Cottus bairdi was the dominant sculpin in the database, age effects on organic residues were statistically examined in this species. Ages ranged from 0 to 8 years, as illustrated by the following age breakdown of the number (N) of paired (tissue-water, tissue-sediment) observations on benzene hexachloride (BHC):

Age (years)	N Tissue-Water	Approx. % of Total	N Tissue-Sediment	Approx. % of Total
0	3	5	3	4
1	2	3	2	3
2	7	12	7	11
2-3	9	15	9	13
3	5	8	7	11
3-4	6	10	6	9
4	11	19	13	19
4-5	5	8	6	9
5	5	8	7	11

Age (years)	N Tissue-Water	Approx. % of Total	N Tissue-Sediment	Approx. % of Total
5-6	2	3	2	3
6	1	2	1	1
6-7	1	2	1	1
7	2	3	3	4
8	1	2	1	1
TOTAL	60	100	68	100

There is a fairly even representation of different ages in the database. Distributions associated with other organic contaminants were similar.

Correlations of organic residues with age did not indicate a strong age relationship for most organic parameters. Neither was percent lipid significantly related to fish age. Thus, it is not surprising that plots of residue relationships with water and sediment variables, using age as a plot symbol, did not suggest any partitioning of relationships according to age class. Examples of these plots are illustrated in Figure 4.6.

Significant age correlations are listed in Table 4.12. These are consistently positive (increasing residue with age) for polyaromatic hydrocarbons ($r = 0.34$ to 0.61), and tetrachlorobenzenes ($r = 0.29$). They are consistently negative (decreasing residue with age) for other chlorinated aromatics and pentachlorophenol. Pesticides exhibit both weak positive and weak negative age relationships.

4.3.6 Food Chain Effects

Food chain effects were examined for Cottus bairdi, a generalized bottom feeder known to consume most of the benthos in the In-place Pollutants database. In general, these fish-benthos correlations were weak or absent. The strongest correlations were for

mirex (r = 0.69), tetrachlorobenzene (r = 0.70) and phenanthrene (r = 0.64). Detection limits for fish and benthos, if they vary from year to year, may be expected to co-vary, and this may account for some of the apparent food chain relationships.

TABLE 4.0: EXAMPLES OF THE USE OF SEDIMENT EXTRACTION TECHNIQUES TO PREDICT THE BIOAVAILABILITY OF SEDIMENT-BOUND METALS TO FRESHWATER BENTHIC INVERTEBRATES (from Campbell et al., 1988)

Species	Organism part	Metal	N[a]	Study type[b]	Sediment extraction procedure	Prediction of metal accumulation (coefficient of determination)[c]	Reference
Filter feeders							
1. Elliptio complanata (mollusc)	Whole	(a) Cu	8	F	• $MgCl_2$ (0.5 M)/pH7 • NaOAc (1 M), HOAc/pH 5 • $NH_2OH \cdot HCl$ (0.04 M), HOAc (25%)/95°C • H_2O_2 (30%), HNO_3/85°C, pH 2 • HF, $HClO_4$ (5:1)/digestion (fresh sediment, ≤70 µm; sequential)	(a) Cu extracted in fractions 1→3 + Fe extracted with $NH_2OH \cdot HCl$ (r^2 = 0.95)	Tessier et al. 1984
	Whole	(b) Zn	8	F		(b) Zn extracted with H_2O_2 + Fe extracted with $NH_2OH \cdot HCl$ (r^2 = 0.79) Zn extracted in fractions 1→3 + Fe extracted with $NH_2OH \cdot HCl$ (r^2 = 0.66)	
	Gills	(c) Pb	8	F		(c) Pb extracted in fractions 1→3 + Fe extracted with $NH_2OH \cdot HCl$ (r^2 = 0.93)	
2. Anodonta grandis (mollusc)	Whole	(a) Cu	6	F	• $MgCl_2$ (0.5 M)/pH 7 • NaOAc (1 M), HOAc/pH 5 • $NH_2OH \cdot HCl$ (0.04 M), HOAc (25%)/95°C • H_2O_2 (30%), HNO_3/85°C, pH 2 • HF, $HClO_4$ (5:1)/digestion (fresh sediment, ≤70 µm; sequential)	(a) Cu extracted in fractions 1→3 + Fe extracted with $NH_2OH \cdot HCl$ (r^2 = 0.85)	Tessier et al. 1982b
	Whole	(b) Zn	6	F		(b) Zn extracted with H_2O_2 + Fe extracted with $NH_2OH \cdot HCl$ (r^2 = 0.81)	
	Gills	(c) Pb	6	F		(c) [Pb/Fe] extracted with $NH_2OH \cdot HCl$ (r^2 = 0.76)	
Deposit feeders							
3. Oligochaetes (unidentified; mainly Limnodrilus hoffmeisteri and Tubifex tubifex)	Whole	(a) Cu	12	F	• Centrifugation • NH_4OAc (1.3 M)/pH 7 • $NH_2OH \cdot HCl$ (0.1 M), HNO_3/pH 2 • H_2O_2 (30%), HNO_3/95°C, pH 2 • HCl (3 M)/80°C • HF (70%), HNO_3/digestion (fresh sediment, ≤2 µm; sequential)	(a) Cu extracted with $NH_2OH \cdot HCl$ (r^2 = 0.85)	Bindra and Hall 1977; Hall and Bindra 1979
		(b) Pb	12	F		(b) total Pb (r^2 = 0.46); Pb extracted with $NH_2OH \cdot HCl$ (r^2 = 0.35)	
		(c) Zn	12	F		(c) NS	

[a] N = number of sites.
[b] Study type: F = field study; L = laboratory study.
[c] NS = no significant correlation between $[M]_{org}$ and $[M]_{sed}$.

TABLE 4.0: EXAMPLES OF THE USE OF SEDIMENT EXTRACTION TECHNIQUES TO PREDICT THE BIOAVAILABILITY OF SEDIMENT-BOUND METALS TO FRESHWATER BENTHIC INVERTEBRATES (from Campbell et al., 1988)

Species	Organism part	Metal	N[a]	Study type[b]	Sediment extraction procedure	Prediction of metal accumulation (coefficient of determination)[c]	Reference
1. Macoma balthica (mollusc)	Whole	(a) Hg	29	F	• HCl (1 M) • NaOH (0.1 M) • H_2O_2 (30%)/60°C • HNO_3 (15 M)/digestion (fresh sediment, ≤100 µm; nonsequential)	(a) Hg extracted with HNO_3 + percentage of organic matter (r^2 = ?)	Langston 1982
	Whole	(b) Zn	28	F	• NH_4OAc (1 M) • $NH_4C_2O_4$ (0.4 M); $H_2C_2O_4$ (0.4 M)/pH 3.3 • HOAc (25%)/pH 2.2 • $NH_2OH \cdot HCl$, HNO_3 (0.01 M)/pH 2 • HCl (1 M) • NH_4OH (1 M)/pH 10 • HNO_3 (15 M)/digestion (fresh sediment, ≤250 µm; nonsequential)	(b) NS	Luoma and Bryan 1979
	Whole	(c) Cd	14	F		(c) Cd extracted with HCl (r^2 = 0.21, log-log)	Bryan 1985
		(d) Ag	15	F		(d) Ag extracted with HCl (r^2 = 0.68, log-log)	
		(e) Zn	16	F	• HCl (1 M) (fresh sediment, ≤100 µm)	(e) Zn extracted with HCl (r^2 = 0.31, log-log)	
		(f) Pb	15	F		(f) [Pb/Fe] extracted with HCl (r^2 = 0.58, log-log)	
		(g) Cu	17	F		(g) NS	

TABLE 4.0: EXAMPLES OF THE USE OF SEDIMENT EXTRACTION TECHNIQUES TO PREDICT THE BIOAVAILABILITY OF SEDIMENT-BOUND METALS TO FRESHWATER BENTHIC INVERTEBRATES (from Campbell et al., 1988)

Species	Organism part	Metal	N[a]	Study type[b]	Sediment extraction procedure	Prediction of metal accumulation (coefficient of determination)[c]	Reference
2. Scrobicularia plana (mollusc)	Whole	(a) Pb	37	F	• NH_4OAc (1 M) • $NH_4C_2O_4$ (0.2 M), $H_2C_2O_4$ • HOAc (25%); HNO_3/pH 2.2 • $NH_2OH \cdot HCl$ (0.1 M), HNO_3 (0.01 M) (fresh sediment, ≤100 µm; nonsequential) • HCl (1 M) • HNO_3 (15 M)/digestion (dried sediment, nonsequential)	(a) [Pb/Fe] extracted with HCl (r^2 = 0.98, linear; 0.88, log-log)	Luoma and Bryan 1978
	Whole	(b) As	75	F	• HCl (1 M) • HOAc (25%) • HNO_3 (15 M)/digestion (fresh sediment, ≤100 µm; nonsequential)	(b) [As/Fe] extracted with HCl (r^2 = 0.93, linear; 0.82, log-log)	Langston 1980
	Whole	(c) Hg	78	F	• HCl (1 M) • NaOH (0.1 M) • H_2O_2 (30%W)/60°C • HNO_3 (15 M)/digestion (fresh sediment, ≤100 µm; nonsequential)	(c) Hg extracted with HNO_3 + percentage of organic matter (r^2 = 0.63)	Langston 1982
	Whole	(d) Zn	40	F	• NH_4OAc (1 M) • $NH_4C_2O_4$ (0.4 M); $H_2C_2O_4$ (0.4 M)/pH 3.3 • HOAc (25%)/pH 2.2 • $NH_2OH \cdot HCl$, HNO_3 (0.01 M)/pH 2 • HCl (1 M) • NH_4OH (1 M)/pH 10 • HNO_3 (15 M)/digestion (fresh sediment, ≤250 µm; nonsequential)	(d) Zn extracted with NH_4OAc (r^2 = 0.38)	Luoma and Bryan

TABLE 4.0: EXAMPLES OF THE USE OF SEDIMENT EXTRACTION TECHNIQUES TO PREDICT THE BIOAVAILABILITY OF SEDIMENT-BOUND METALS TO FRESHWATER BENTHIC INVERTEBRATES (from Campbell et al., 1988)

Species	Organism part	Metal	N[a]	Study type[b]	Sediment extraction procedure	Prediction of metal accumulation (coefficient of determination)[c]	Reference
3. Nereis diversicolor (polychaete)	Whole	(a) As	82	F	• HCl (1 M) • HOAc (25%) • HNO_3 (15 M)/digestion (fresh sediment, ≤100 µm; nonsequential)	(a) [As/Fe] extracted with HCl (r^2 = 0.55, log-log)	Langston 1980
	Whole	(b) Co	37	F	• NH_4OH (1 M)/pH 11.6 • NH_4OAc (1 M)/pH 7 • $NH_4C_2O_4$ (0.4 M), $H_2C_2O_4$ (0.4 M)/pH 3.3 • HOAc (25%)/pH 2.2 • HNO_3 (15 M)/digestion (fresh sediment, ≤100 µm; nonsequential)	(b) Co extracted with HCl (r^2 = 0.66, log-log)	Luoma and Bryan 1982
	Whole	(c) Ag	37	F		(c) Ag extracted with HCl (r^2 = 0.81, log-log)	
	Whole	(d) Pb	37	F		(d) Pb extracted with HNO_3 (r^2 = 0.72, log-log)	
	Whole	(e) Cu	37	F		(e) Cu extracted with HNO_3 (r^2 = 0.72, log-log)	
	Whole	(f) Ag	38	F	• HCl (1 M) (fresh sediment, ≤100 µm)	(f) Ag extracted with HCl (r^2 = 0.62, log-log)	Bryan 1985

[a] N = number of sites.
[b] Study type: F = field survey.
[c] NS = no significant correlations between $[M]_{org}$ and $[M]_{sed}$.

TABLE 4.1: SPEARMAN CORRELATION OF METALS IN FISH WITH BOTTOM WATER AND BULK SEDIMENT CONCENTRATIONS

Metal	Water Normalized by:				Sediment Normalized by:			
	*	FeOx	MnOx	TOC	*	FeOx	MnOx	TOC
Copper	-	-	-	-	-	0.36	0.33	0.47
Chromium	-	-	-	-	-	0.31	0.33	0.33
Arsenic	NV	NV	NV	NV	-	-	-	-
Manganese	0.39	0.26	0.38	-	0.40	0.43	0.59	0.61
Aluminum	-	-	-	-	-	-	-	0.49
Iron	-	-	-	-	-	0.35	0.53	0.42
Cadmium	-	-	0.18	-	-	-	-	0.21
Nickel	-	-	-	-	-	-	-	0.29
Lead	0.34	-	-	0.40	-	0.24	0.30	0.37
Zinc	0.24	-	-	-	-	-	-	0.74
Mercury	-			-	-			0.48

* Indicates no normalization.

\- Indicates non-significant (p greater than 0.05) or negative coefficient.

NV Indicates no variance (i.e., constant contaminant value).

TABLE 4.2: SPEARMAN CORRELATION OF METALS IN BENTHOS WITH BOTTOM WATER AND BULK SEDIMENT CONCENTRATIONS

Metal	Water Normalized by:				Sediment Normalized by:			
	*	FeOx	MnOx	TOC	*	FeOx	MnOx	TOC
Copper	-	-	-	-	0.25	-	-	0.58
Chromium	-	-	-	-	-	0.26	-	0.43
Arsenic	-	-	-	-	0.20	0.43	0.33	0.52
Manganese	0.42	0.46	0.59	0.51	-	-	0.21	0.48
Aluminum	-	-	-	-	-	-	-	0.27
Iron	-	-	-	-	-	-	0.19	0.57
Cadmium	-	-	-	-	-	-	-	0.29
Nickel	-	0.24	0.47	-	-	-	-	0.55
Lead	-	-	-	-	-	-	-	0.35
Zinc	-	-	-	-	0.26	-	-	0.79
Mercury	-			-	0.24			0.65

* Indicates no normalization.

- Indicates non-significant (p greater than 0.05) or negative coefficient.

TABLE 4.3: SPEARMAN CORRELATION OF METALS IN FISH AND BENTHOS WITH CONCENTRATION IN F4 SEDIMENT FRACTION

	FISH				BENTHOS			
	Sediment Normalized by:				Sediment Normalized by:			
Metal	*	FeOx	MnOx	TOC	*	FeOx	MnOx	TOC
Copper	0.71	0.81	0.79	0.40	0.27	0.54	0.29	0.29
Chromium	0.45	0.45	0.28	0.48	0.47	0.30	-	0.26
Arsenic	0.67	0.73	0.73	0.53	-	0.41	0.34	-
Manganese	0.23	0.75	0.67	-	-	0.29	0.28	-
Aluminum	-	0.48	0.39	-	0.23	0.47	0.44	-
Iron	0.23	0.79	0.72	-	0.22	0.87	0.54	0.20
Cadmium	0.61	-	-	-	-	-	-	-
Nickel	-	-	-	-	-	0.49	0.43	0.35
Lead	-	-	-	-	0.30	0.49	0.57	0.38
Zinc	-	0.86	0.56	0.30	-	0.40	0.46	0.26

* Indicates no normalization.

\- Indicates non-significant (p greater than 0.05) or negative coefficient.

TABLE 4.4: SHEA AND TESSIER MODELS AS PREDICTORS OF HEAVY METALS IN FISH

Metal	Shea Model[1]					Tessier Model[2]		
	a	k_1	k_2	k_3	R	a	k	R
Copper	6.9	-0.007	-0.0002	-0.0002	0.52	-	-	-
Chromium	-	-	-	-	-	0.002	739	0.30
Arsenic	82.8	-0.139	0.001	-0.0004	0.35	-	-	-
Manganese	-	-	-	-	-	1.4	38.9	0.36
Aluminum	-	-	-	-	-	-	-	-
Iron	-	-	-	-	-	-	-	-
Cadmium	-63	-0.08	0.01	0.002	0.37	-	-	-
Nickel	-	-	-	-	-	-0.62	1.127	0.30
Lead	10	0.22	0.003	0.002	0.42	-	-	-
Zinc	14	-0.03	-0.002	0.002	0.57	-	-	-

[1] Shea Model:
$$C_b = \frac{C_s}{a + k_1\,MnOx + k_2\,FeOx + k_3\,TOC}$$

[2] Tessier Model:
$$C_b = a + k\,\frac{F1 + F2 + F4}{FeOx}$$

Notes: FeOx = Fe in (F2 + F4); MnOx = Mn in (F2 + F4).
All concentration units are ug/g.
Underlined model coefficients make a significant (p less than 0.05) contribution to the model.
- Indicates no significant fit of model (p greater than 0.05).

TABLE 4.5: SHEA AND TESSIER MODELS AS PREDICTORS OF HEAVY METALS IN BENTHOS

	Shea Model[1]					Tessier Model[2]		
Metal	a	k_1	k_2	k_3	R	a	k	R
Copper	-	-	-	-	-	-	-	-
Chromium	4.53	-0.206	0.012	0.0007	0.46	-	-	-
Arsenic	-3.85	0.02	-0.002	0.0007	0.59	-	-	-
Manganese	-	-	-	-	-	-	-	-
Aluminum	-	-	-	-	-	-	-	-
Iron	36.8	-0.12	0.008	0.0004	0.36	-	-	-
Cadmium	17.8	0.014	-0.001	0.0001	0.30	-	-	-
Nickel	-	-	-	-	-	-	-	-
Lead	133	0.366	-0.03	0.0009	0.36	-	-	-
Zinc	-	-	-	-	-	-	-	-

[1] Shea Model: $$C_b = \frac{C_s}{a + k_1\,MnOx + k_2\,FeOx + k_3\,TOC}$$

[2] Tessier Model: $$C_b = a + k\,\frac{F1 + F2 + F4}{FeOx}$$

Notes: FeOx = Fe in (F2 + F4); MnOx = Mn in (F2 + F4).

All concentration units are ug/g.

Underlined model coefficients make a significant (p less than 0.05) contribution to the model.

- Indicates no significant fit of model (p greater than 0.05).

TABLE 4.6: SPEARMAN CORRELATION OF ASH-CORRECTED METALS IN BENTHOS WITH CONCENTRATIONS IN BOTTOM WATER AND F4 SEDIMENT FRACTIONS

	Water Normalized by:				Sediment Normalized by:			
Metal	*	FeOx	MnOx	TOC	*	FeOx	MnOx	TOC
Copper	-	-	-	-	-	0.48	0.43	-
Chromium	-	-	-	-	-	-	-	-
Arsenic	-	-	-	-	-	0.33	0.30	-
Manganese	0.34	0.52	0.58	0.46	-	-	-	-
Aluminum	-	-	-	-	-	-	-	-
Iron	-	-	-	-	-	-	-	-
Cadmium	-	-	-	-	-	-	-	0.28
Nickel	0.44	0.43	0.48	0.38	-	0.28	0.24	0.28
Lead	-	-	-	-	0.31	0.43	0.40	0.36
Zinc	-	-	-	-	-	0.28	0.33	-
Mercury	-			-	-			-

* Indicates no normalization.

\- Indicates non-significant (p greater than 0.05) or negative coefficient.

TABLE 4.7: SPEARMAN CORRELATION OF CHLOROPHENOLS AND CHLOROAROMATICS IN FISH WITH BOTTOM WATER AND BULK SEDIMENT CONCENTRATIONS

	Fish vs. Water Normalization				Fish vs. Sediment Normalization			
		Tissue	Water			Tissue	Sediment	
Organic Compound	None	Lipid	TOC	Both	None	Lipid	TOC	Both
2,4,5-Trichlorophenol	NV	0.39	-	0.42	NV	NV	NV	NV
2,4,6-Trichlorophenol	0.61	-	0.34	-	NV	NV	NV	NV
2,3,4,5-Tetrachlorophenol	0.70	-	-	-	NV	NV	NV	NV
2,3,5,6-Tetrachlorophenol	0.94	-	0.55	-	NV	NV	NV	NV
Pentachlorophenol	-	-	-	-	-	-	-	-
1,2,4-Trichlorobenzene	NV	NV	NV	NV	NV	0.16	-	-
1,2,3-Trichlorobenzene	-	-	-	-	-	-	-	-
Hexachlorobutadiene	NV	NV	NV	NV	-	-	-	-
Octachlorostyrene	NV	NV	NV	NV	0.26	0.53	-	0.47

- Indicates non-significant (p greater than 0.05) or negative coefficient.

NV indicates no variance (i.e., constant contaminant value).

TABLE 4.8: SPEARMAN CORRELATION OF CHLOROPHENOLS AND CHLOROAROMATICS IN BENTHOS WITH BOTTOM WATER AND BULK SEDIMENT CONCENTRATIONS

	Fish vs. Water Normalization				Fish vs. Sediment Normalization			
		Tissue	Water			Tissue	Sediment	
Organic Compound	None	Lipid	TOC	Both	None	Lipid	TOC	Both
2,4,5-Trichlorophenol	-	-	0.37	0.37	NV	NV	NV	NV
2,4,6-Trichlorophenol	-	-	-	-	0.74	0.60	0.43	0.41
2,3,4,5-Tetrachlorophenol	0.61	0.51	-	-	NV	NV	NV	NV
2,3,5,6-Tetrachlorophenol	0.57	0.41	-	-	NV	NV	NV	NV
Pentachlorophenol	-	-	-	-	-	-	-	-
1,2,4-Trichlorobenzene	NV	NV	NV	NV	NV	0.25	-	-
1,2,3-Trichlorobenzene	0.12	0.17	0.17	0.39	-	-	-	-
Hexachlorobutadiene	NV	NV	NV	NV	-	-	-	-
Octachlorostyrene	NV	NV	NV	NV	NV	-	-	-

- Indicates non-significant (p greater than 0.05) or negative coefficient.

NV indicates no variance (i.e., constant contaminant value).

TABLE 4.9: SPEARMAN CORRELATION OF PCB AND PESTICIDES IN FISH WITH BOTTOM WATER AND BULK SEDIMENT CONCENTRATIONS

	Fish vs. Water Normalization				Fish vs. Sediment Normalization			
		Tissue	Water			Tissue	Sediment	
Organic Compound	None	Lipid	TOC	Both	None	Lipid	TOC	Both
Hexachlorobenzene	NV	NV	NV	NV	-	0.20	0.20	0.26
Heptachlor Epoxide	NV	NV	NV	NV	-	-	-	-
Mirex	NV	NV	NV	NV	0.15	NV	-	NV
a-BHC	-	-	-	-	NV	NV	NV	NV
g-BHC	-	-	-	-	NV	NV	NV	NV
a-Chlordane	NV	NV	NV	NV	-	-	-	-
g-Chlordane	-	0.17	-	0.13	-	-	-	-
PCB	NV	NV	NV	NV	-	0.21	-	-
p,p-DDE	NV	NV	NV	NV	-	0.31	0.31	0.29
p,p-DDD	NV	NV	NV	NV	-	-	-	-
p,p-DDT	NV	NV	NV	NV	-	-	-	-
o,p-DDT	NV	NV	NV	NV	-	0.19	-	-
Endosulphan I	NV	NV	NV	NV	-	-	-	-
Endosulphan II	NV	NV	NV	NV	-	-	-	-
Dieldrin	NV	NV	NV	NV	0.30	NV	0.28	NV
Endrin	NV	NV	NV	NV	-	0.19	-	-
Endosulphan SO_4	NV	NV	NV	NV	-	-	-	-
DMDT	NV	NV	NV	NV	0.29	0.62	0.62	0.61
b-BHC	-	-	-	-	-	-	-	-

- Indicates non-significant (p greater than 0.05) or negative coefficient.

NV indicates no variance (i.e., constant contaminant value).

TABLE 4.10: SPEARMAN CORRELATION OF PCB AND PESTICIDES IN BENTHOS WITH BOTTOM WATER AND BULK SEDIMENT CONCENTRATIONS

	Benthos vs. Water Normalization				Benthos vs. Sediment Normalization			
		Tissue	Water			Tissue	Sediment	
Organic Compound	None	Lipid	TOC	Both	None	Lipid	TOC	Both
Hexachlorobenzene	-	-	-	-	0.31	-	-	-
Heptachlor Epoxide	NV	NV	NV	NV	-	-	-	-
Aldrin	0.59	0.17	0.17	0.09	NV	NV	NV	NV
a-BHC	-	-	-	-	NV	NV	NV	NV
g-BHC	-	-	-	-	NV	NV	NV	NV
a-Chlordane	-	-	-	-	0.28	-	-	-
g-Chlordane	-	0.15	-	-	0.30	-	0.19	-
PCB	-	-	-	NV	0.19	-	0.32	0.21
oxy-Chlordane	NV	NV	NV	NV	-	-	-	-
p,p-DDE	NV	NV	NV	NV	-	0.25	0.20	0.35
p,p-DDD	NV	NV	NV	NV	0.28	0.30	0.28	0.22
p,p-DDT	-	-	-	-	-	-	-	-
o,p-DDT	NV	NV	NV	NV	-	-	-	0.32
Endosulphan I	NV	NV	NV	NV	0.25	-	0.21	-
Endosulphan II	NV	NV	NV	NV	-	-	-	-
Dieldrin	0.29	0.29	0.29	NV	-	-	-	-
Endrin	NV	NV	NV	NV	-	-	-	-
Endosulphan SO_4	0.15	0.17	-	-	-	-	0.15	-
DMDT	NV	NV	NV	NV	0.50	0.28	0.45	0.27
b-BHC	-	-	-	-	-	-	-	-

- Indicates non-significant (p greater than 0.05) or negative coefficient.

NV indicates no variance (i.e., constant contaminant value).

TABLE 4.11: SPEARMAN CORRELATION OF POLYAROMATIC HYDROCARBONS IN FISH AND BENTHOS WITH BULK SEDIMENT CONCENTRATIONS

	Benthos vs. Water Normalization				Benthos vs. Sediment Normalization			
		Tissue	Water			Tissue	Sediment	
Organic Compound	None	Lipid	TOC	Both	None	Lipid	TOC	Both
Dibenzanthracene	-	-	-	-	-	0.51	0.44	0.55
Benzoperylene	-	-	-	-	-	0.54	0.50	0.61
Naphthalene	ID	ID	ID	ID	-	-	0.50	0.52
Acenaphthylene	NV	NV	NV	NV	NV	-	-	0.67
Acenaphthene	ID	ID	ID	ID	-	-	-	-
Fluorene	NV	0.54	0.24	0.53	-	-	-	-
Phenanthrene	-	-	-	-	0.49	0.56	0.63	0.70
Anthracene	-	-	0.54	0.53	-	-	-	-
Fluoranthene	0.50	-	0.49	0.45	0.72	0.73	0.64	0.64
Pyrene	0.64	0.54	0.67	0.59	0.64	0.65	0.55	0.56
Benzo(a)anthracene	-	-	-	-	0.71	0.76	0.75	0.71
Chrysene	-	-	0.53	-	0.68	0.72	0.58	0.64
Benzo(a)pyrene	-	-	-	-	0.42	0.45	0.63	0.73
Idenopyrene	-	-	-	-	-	0.43	0.53	0.56
Benzofluoranthene	NV	ID	ID	ID	0.13	0.56	0.63	0.61

- Indicates non-significant (p greater than 0.05) or negative coefficient.

NV indicates no variance (i.e., constant contaminant value).

ID indicates insufficient data (n less than 10).

TABLE 4.12: SIGNIFICANT[1] AGE RELATIONSHIPS OF LIPID NORMALIZED ORGANIC RESIDUES IN SCULPINS (Cottus bairdi)

Parameter	Correlation	Parameter	Correlation
Pesticides (n = 71)		**Chlorinated Aromatics (n = 47)**	
Heptachlor	-0.24	Hexachloroethene	-0.42
Mirex	-0.24	1,3,5-Trichlorobenzene	-0.31
p,p-DDE	0.35	1,2,4-Trichlorobenzene	-0.31
p,p-DDT	0.33	2,6,a-Trichlorotoluene	-0.31
DMDT	0.38	1,2,3,5-Tetrachlorobenzene	0.29
		1,2,4,5-Tetrachlorobenzene	0.29
PAHs (n = 45)		**Chlorophenols (n = 49)**	
Dibenzanthracene	0.34	Pentachlorophenol	-0.38
Benzoperylene	0.59		
Phenanthrene	0.51		
Fluorene	0.37		
Anthracene	0.37		
Fluoranthene	0.61		
Pyrene	0.42		
Chrysene	0.55		
Benzo(a)pyrene	0.35		
Idenopyrene	0.59		

[1] Positive or negative correlation coefficients (p less than 0.05).

TABLE 4.13: SIGNIFICANT[1] FOOD CHAIN RELATIONSHIPS OF LIPID NORMALIZED ORGANIC RESIDUES IN SCULPINS (Cottus bairdi)

Parameter	Correlation	Parameter	Correlation
Pesticides (n = 59)		**Chlorinated Aromatics (n = 44)**	
a-BHC	0.41	Hexachloroethane	0.33
Mirex	0.69	1,2,3,5-Tetrachlorobenzene	0.70
p,p-DDT	0.43	1,2,4,5-Tetrachlorobenzene	0.70
DMDT	0.65	1,2,3,4-Tetrachlorobenzene	0.37
PAHs (n = 14)		**Chlorophenols (n = 25)**	
Phenanthrene	0.64	None	

[1] Positive correlation coefficients (p less than 0.05).

Figure 4.1 : FISH METAL RESIDUES VS. IRON-NORMALIZED F4 SEDIMENT
(Plot by species code)

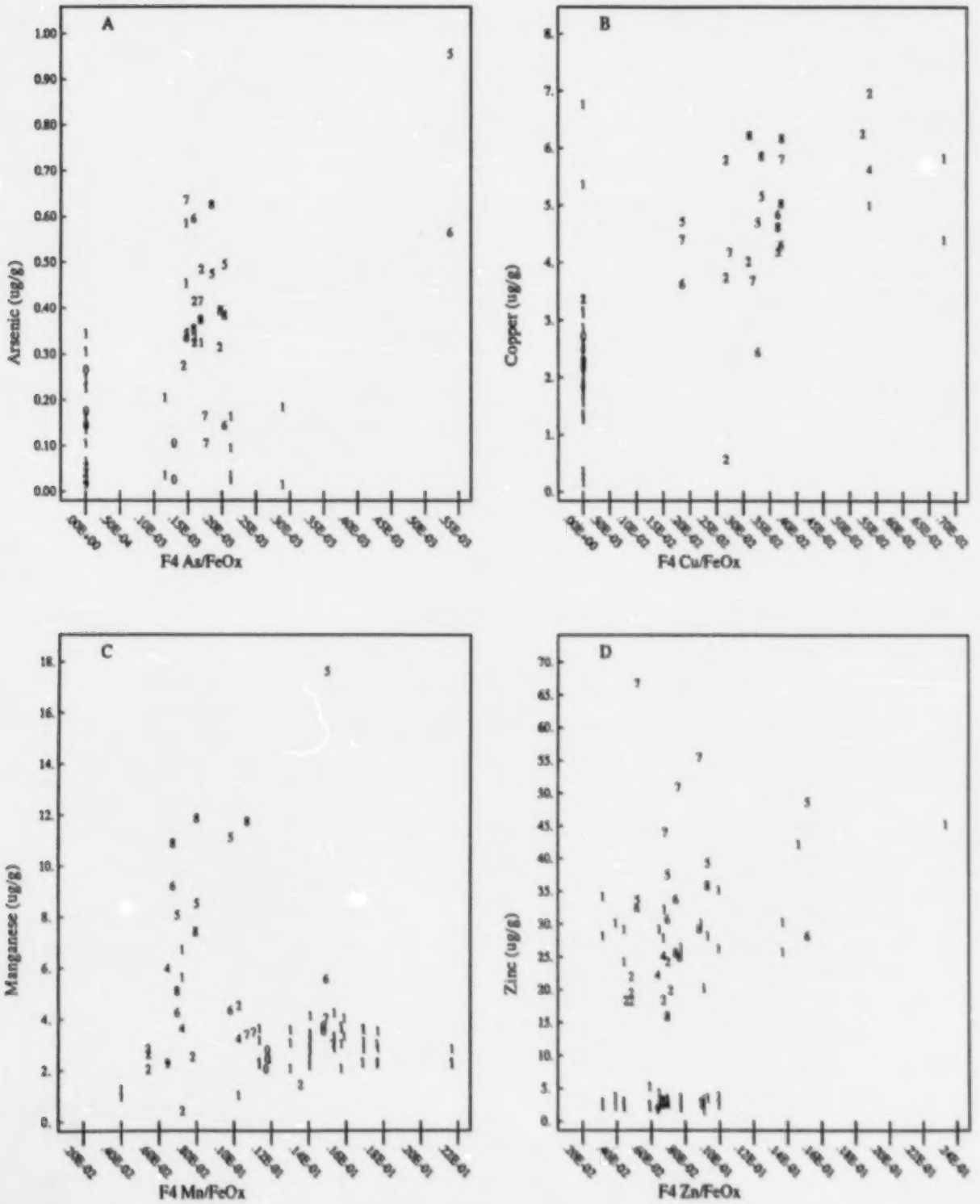


Figure 4.2 : FISH COPPER RESIDUE VS. SHEA MODEL PREDICTION
(Plot by species (left) and age code (right))

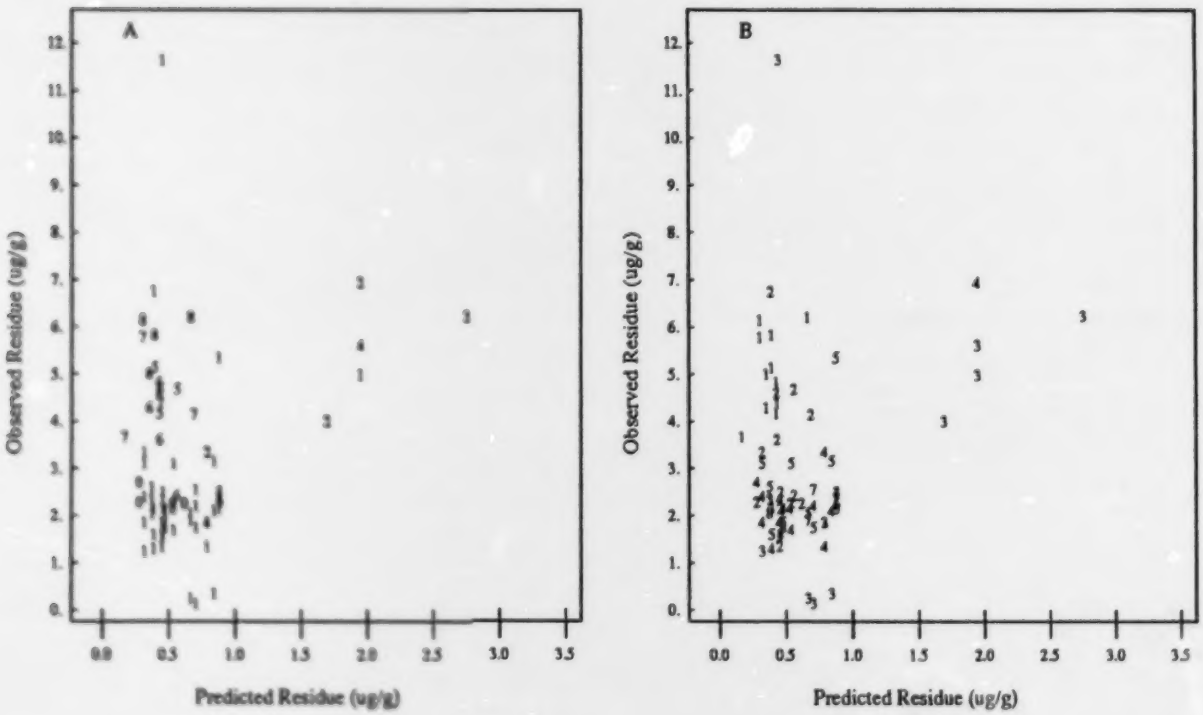


Figure 4.3 : FISH METAL RESIDUES VS. IRON-NORMALIZED F4 SEDIMENT
(Plot by age code)

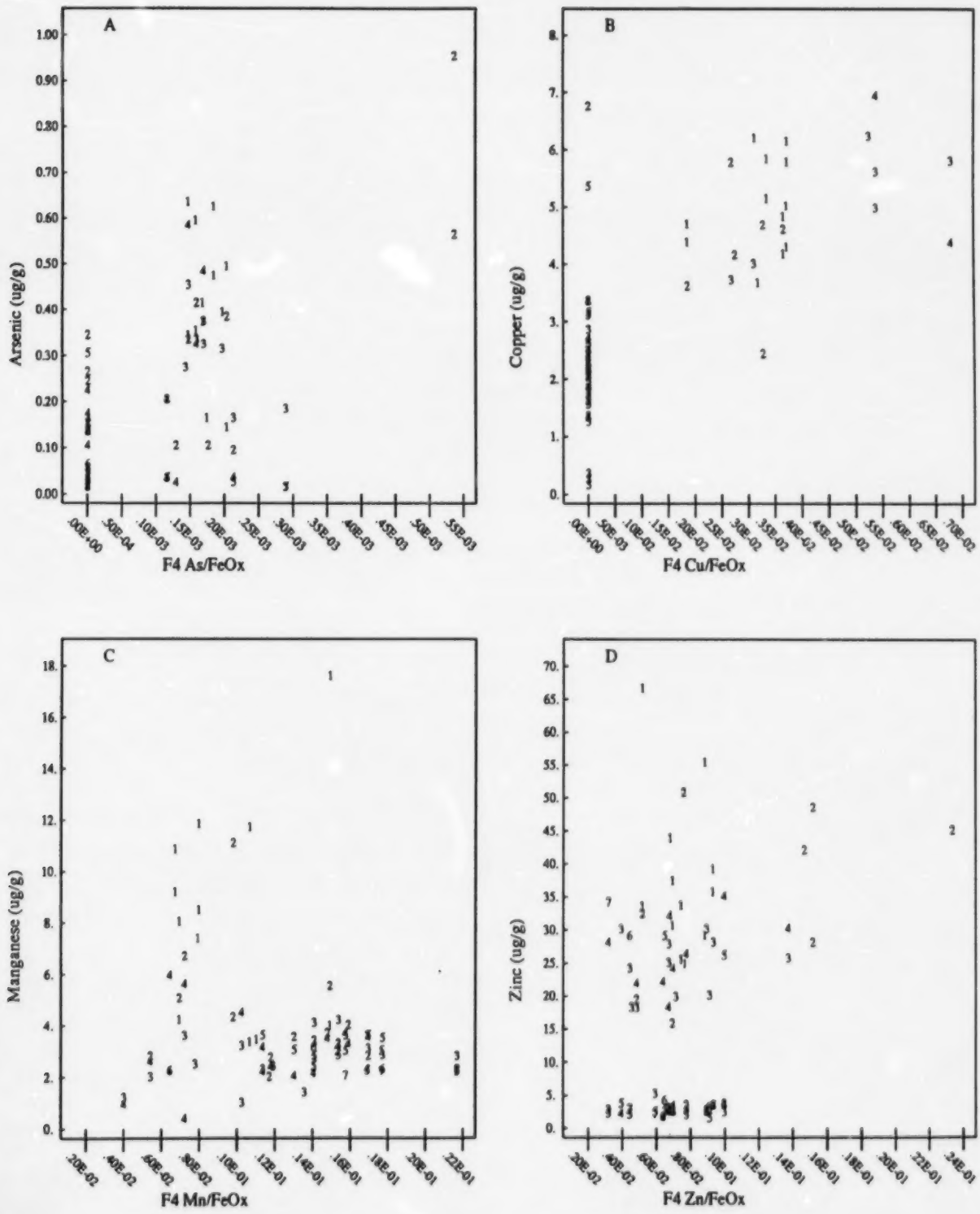


Figure 4.4 : CHLOROPHENOL RESIDUES VS. BOTTOM WATER
Fish Chlorophenol Residues (Plot by age code (top))
Benthos Chlorophenol Residues (Plot by species code (bottom))

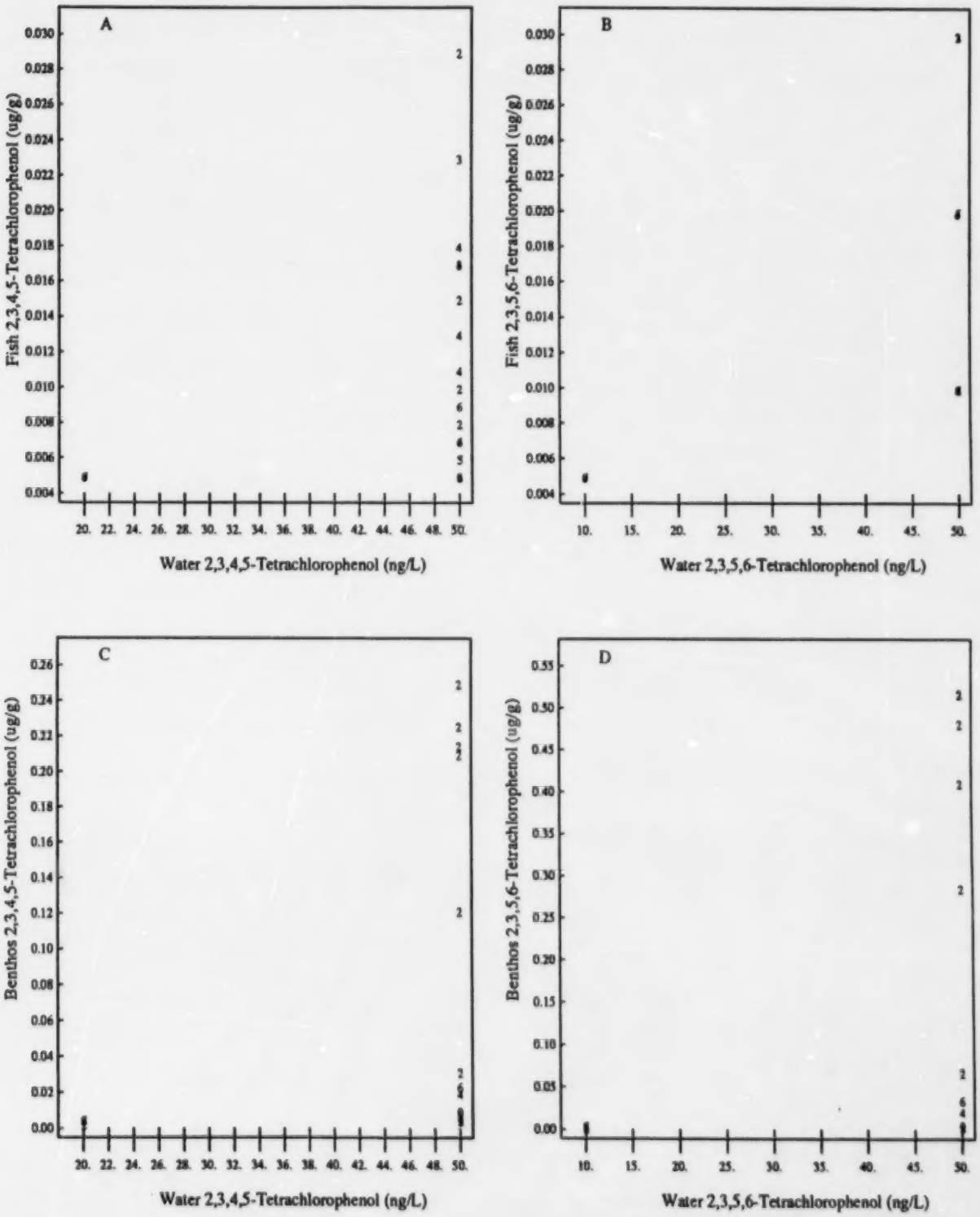


Figure 4.5 : BENTHOS PAH RESIDUES (LIPID-NORMALIZED) VS. BULK SEDIMENT (TOC-NORMALIZED)
(Plot by species code)

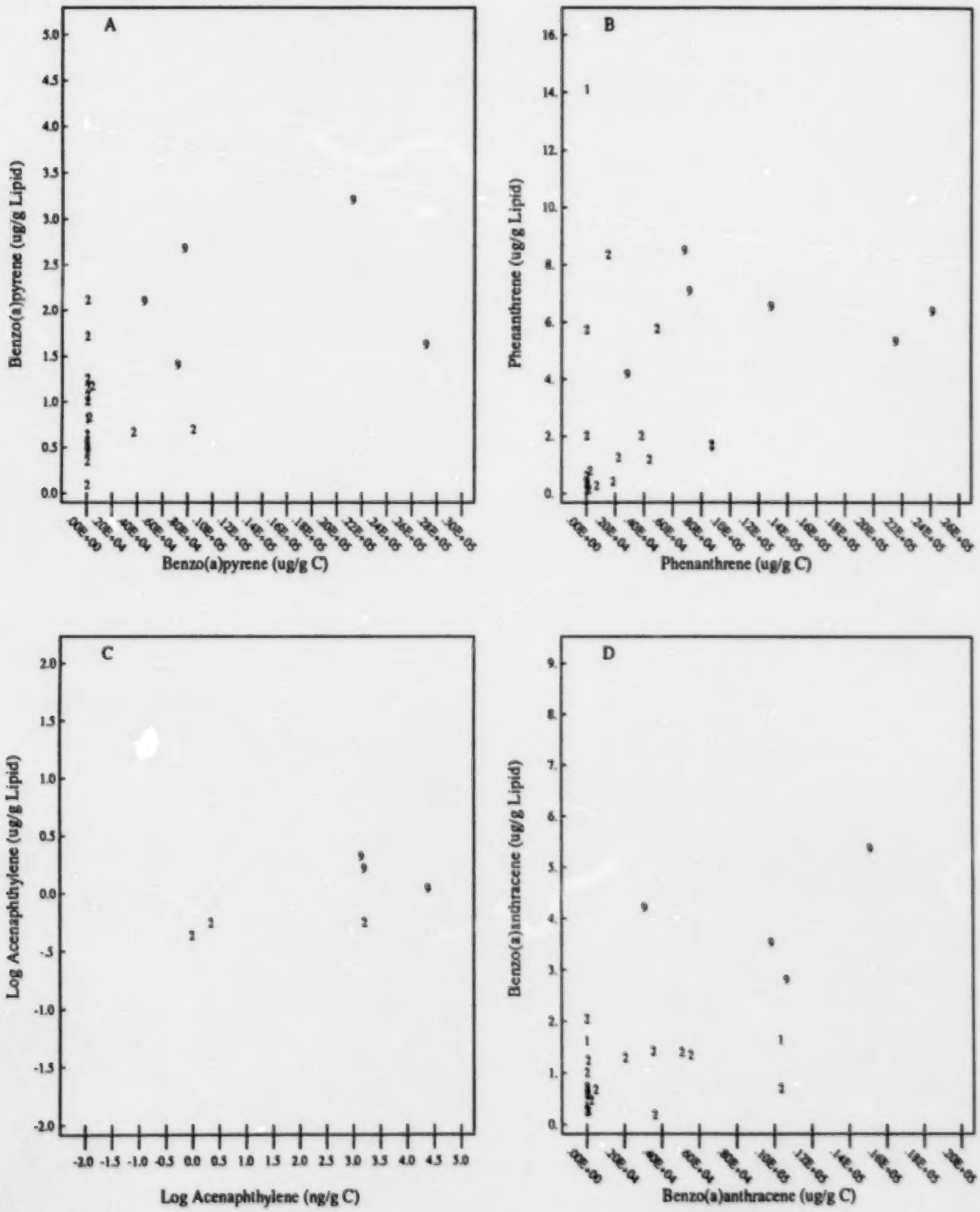
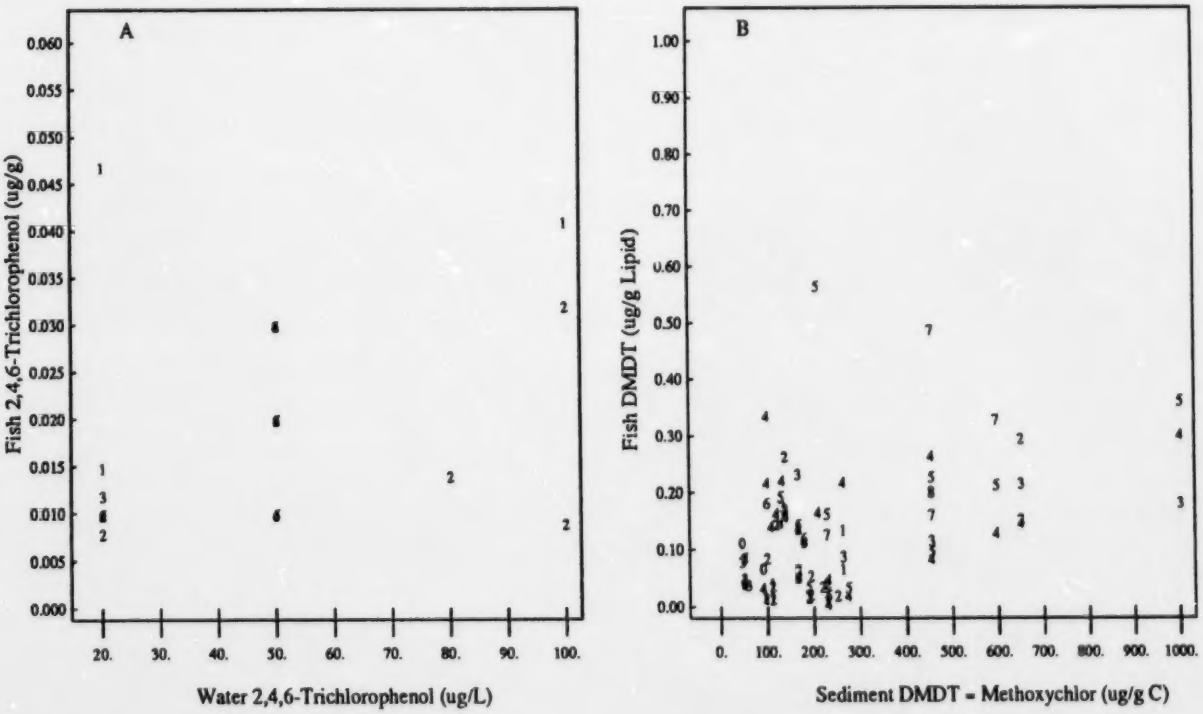


Figure 4.6 : AGE EFFECTS ON FISH ORGANIC RESIDUE RELATIONSHIPS
2,4,6-Trichlorophenol vs. Bottom Water (left)
DMDT (Lipid-Normalized) vs. Sediment (TOC-Normalized) (right)



5.0 CONCLUSIONS

Based on statistical evaluation of residue relationships in the In-place Pollutants database, as well as review of published literature on other similar studies, the following conclusions may be drawn.

1. Heavy metal residues in fish and benthos are poorly correlated with bottom-water and bulk sediment concentrations prior to normalization. Total organic carbon is the best normalizing factor for bulk sediments, but provides only modest improvement in residue relationships.

2. The F4 sediment fraction is better correlated than bulk sediment with metal residues in biota, and is best normalized by iron oxide. Fish display better residue relationships than benthos (e.g., r = 0.73 (As), 0.75 (Mn), 0.79 (Fe), 0.81 (Cu), 0.86 (Zn)).

3. The complex models of Shea (1988) and Tessier et al. (1984) are generally inferior to the normalized F4 sediment fraction as metal residue predictors. The Shea model was superior only for arsenic in benthos.

4. Tetrachlorophenol residues in fish and benthos are better correlated with bottom water concentrations (not normalized) than with sediments. Fish display better residue relationships than benthos (e.g., r = 0.70 to 0.94).

5. Organochlorine pesticide, PCB and chloroaromatic residues in fish and benthos are very poorly correlated with bottom water and sediment concentrations. For many of these compounds, water concentrations were invariable, at or below detection limits.

6. Polyaromatic hydrocarbon (PAH) residues in fish and benthos are correlated with sediment concentrations. Lipid normalization of residues and TOC

normalization of sediment provides the best results. These relationships are better in benthos than fish (e.g., r = 0.67 (acenaphthylene), 0.70 (phenanthrene), 0.71 (benzo(a)anthracene), 0.73 (benzo(a)pyrene)).

7. There is little evidence of taxonomic differences in residue relationships within the fish or benthic datasets. However, fish residues are generally more predictable for metals and chlorophenols, while benthic residues are more predictable for PAHs.

8. Taxon-specific dry/wet weight conversion of residue data provides little advantage within the current database, particularly in view of the database dominance by oligochaetes and sculpins.

9. In the sculpin database, neither percent lipid content nor contaminant residues (organics lipid normalized) are strongly age related.

10. Ash-correction of residue data provides little, if any, advantage for benthos, and is not appropriate for fish.

11. Food chain effects are generally weak or absent based on sculpin-benthos residue correlations, and may be affected by covariance of residue detection limits, particularly for organics.

6.0 RECOMMENDATIONS

Recommendations for future In-place Pollutants monitoring must depend on the current perception of program objectives; however, the following suggestions would focus the program on samples and measurements that have proven most useful in the past for description of contaminant residue relationships, and on procedural changes that would permit exploration of possible improvements in these relationships.

1. Focus metal and chlorophenol analyses on bottom-dwelling fish, particularly sculpins, since their residues have been better related to water and sediment concentrations than have residues of benthic organisms. Focus PAH analysis on benthos.

2. Measure metal concentrations in bulk sediments and F4 sediment fractions, along with TOC, iron oxides and manganese oxides (direct measurement of oxides). Metals measured in other sediment fractions and interstitial water have contributed little to residue relationships.

3. In view of the poor metal residue relationships with current sediment fractions other than F4, different or modified extraction procedures could be tried. One such extraction procedure uses a mild, inorganic acid such as 0.1 N HCl. This extract was used in an early and successful study by Luoma and Bryan (1978) on lead uptake of marine bivalues.

4. Record the dry-weight percent of each bulk sediment sample that consists of the size fraction subjected to geochemical partitioning, to permit expression of geochemical data on a bulk sediment basis.

5. Record fresh and dry weights of all biological samples, to permit sample-specific adjustment of weight basis.

7.0 REFERENCES

Andrews, D. 1988. Availability of Zinc to Benthic Organisms from Sediment Fractions. Report to the Ontario Ministry of the Environment by Beak Consultants Limited.

Andrews, D. 1989. An autoradiographic technique to study the uptake and movement of contaminants in benthic invertebrates (subm. Can. J. Fish. Aquat. Sci.).

Andrews, D., R.D. Evans and J. Cornett. 1985. Concentration Factors and Bioavailability of Cobalt-60 to Benthic Deposit-feeders. Report to Atomic Energy of Canada Ltd.

ASTM. 1985. ASTM Standards on Precision ans Bias for Various Applications, 2nd Edition. American Society for Testing and Materials, Philadelphia.

Batelle Pacific Northwest Laboratories (Batelle). 1988. Interim Sediment Quality Criteria Values for Non-polar Hydrophobic Organic Compounds. Report to the U.S. Environmental Protection Agency.

Beak Consultants Limited (BEAK). 1987. Development of Sediment Quality Objectives - Phase I: Options. Ontario Ministry of the Environment, Toronto.

Beak Consultants Limited (BEAK). 1988. Development of Sediment Quality Guidelines - Phase II: Guideline Development. Ontario Ministry of the Environment, Toronto.

Bindra, K.S. and K.J. Hall. 1977. Geochemical partitioning of trace metals in sediments and factors affecting bioaccumulation in benthic organisms. Unpublished report prepared for NRC Ottawa (Contract #032-1082/6073). 59 pp.

Bolton, H.S., R.J. Breteler, B.W. Vigon, J.A. Scanlon and S.L. Clark. 1985. National Perspective on Sediment Quality. Report to the U.S. EPA, by Batelle Washington Environmental Program Office.

Borgmann, U., W.P. Norwood and K.M. Ralph. 1989. Chronic toxicity and bioaccumulation of 2,5,2',5'- and 3,4,3',4'-Tetrachlorobiphenyl and Aroclor 1242 in the Amphipod Hyallela azteca. Arch. Environ. Contam. Toxicol. 19

Borgmann, U. and D.M. Whittle. 1983. Particle size conversion efficiency and contaminat concentrations in Lake Ontario biota. Can. J. Fish. Aquat. Sci. 40: 328-336.

Bryan, G.W. 1985. Bioavailability and effects of heavy metals in marine deposits. In: Wastes in the Sea. Vol. 6. Near-short Waste Disposal. Eds. B. Ketchum, J. Capuzzo, W. Burt, I. Duedall, P. Park and D. Kester. J. Wiley and Sons, New York.

Bryan, G.W. 1979. Bioaccumulation of marine pollutants. J. Mar. Biol. Ass: U.K. 59: 85-107.

Bryan, G.W. and H. Uysal. 1978. Heavy metals in the burrowing bivalve Scorbicularia plana from the Tamar Estuary in relation to environmental levels. J. Mar. Biol. Ass. U.K. 58: 89-108.

Bryan, G.W. and L.G. Hummerstone. 1977. Indicators of heavy-metal contamination in the Looe Estuary (Cornwall) with particular regard to silver and lead. J. Mar. Biol. Ass. U.K. 57: 75-92

Calmano, W. and U. Forstner. 1983. Chemical extraction of heavy metals in polluted river sediments in Central Europe. Sci. Total Environ. 28: 77-90

Campbell, J.H. and R.D. Evans. 1987. Inorganic and organic ligand binding of lead and cadmium and resultant implications for bioavailability. Sci. Total Environ. 62: 219-227.

Campbell, P.G.C., A.G. Lewis, P.M. Chapman, A.A. Crowder, W.K. Fletcher, B. Imber, S.N. Luoma, P.M. Stokes and M. Winfrey. 1988. Biologically Available Metals in Sediments. National Research Council of Canada Special Rpt. 27694.

Chapman, P.M. 1985. Effects of gut sediment contents on measurements of metal levels in benthic invertebrates - a cautionary note. Bull. Environ. Contam. Toxicol. 35: 345-347

Chapman, P.M., L.M. Churchland, P.A. Thomson and E. Michnowsky. 1980. Heavy metal studies with oligochaetes. In: Eds. R.O. Brinkhurst, D.G. Cook. Aquatic Oligochaete Biology. Plenum.

Cohen, A.C., Jr. 1961. Tables for maximum likelihood estimates: singly truncated and singly censored samples. Technometrics 3:535-541.

Creceluis, E.A., J.M. Augenfeld, D.L. Woodruff and J.W. Anderson. 1980. Bull. Environ. Contam. Toxiol. 25: 337-344.

Davies-Colley, R.J., P.O. Nelson and K.J. Williamson. 1984. Environ. Sci. Technol. 18: 491.

Dean, J.M. 1974. The accumulation of ^{65}Zn and other radionuclides by tubificid worms. Hydrobiologia 45: 33-38.

DiToro, D.M., F. Harris, E. Jenne, S. Karickhoff and W. Lick. Synopsis of discussion session 2. Environmental fate and compartmentalization. In "Fate and Effects of Sediment-Bound Chemicals in Aquatic Systems". Dickson, K.L., Maki, A.W. and Brungs, W.A., eds. Pergamon Press. New York.

Elwood, J.W., S.G. Hildebrand snf J.J. Beaucamp. 1976. Contribution of gut contents to the concentration and body burden of elements in Tipula spp. from a spring-fed stream. J. Fish. Res. Bd. Can. 33: 1930-1938.

Environmental Protection Agency (EPA). 1980. Upgrading Environmental Radiation Data. EPA 520/1-80-012. Office of Radiation Programs. U.S.EPA, Washington, D.C.

Evans, R.D., D. Andrews and R.J. Cornette. 1988. Chemical fractionation and bioavailability of Cobalt-60 to Benthic deposit feeders. Can. J. Fish Aquat. Sci. 45: 228-236.

Forstner U. and G.T.W. Wittman. 1983. Metal Pollution in the Environment. Springer-Verlag, New York, 486 pp.

Forstner, U. 1982. Accumulative phases for heavy metals in limnic sediments. In: Sediments and Freshwater Interactions, Ed. P.G. Sly. Hydrobiologia 91: 269-284.

Gibbs, R.J. 1973 Mechanisms of trace metal transport in rivers. Science 180: 71-73.

Gilbert, R.O. 1987. Statistical Methods of Environmental Pollution Monitoring. Van Nostrand Reinhold Co., New York.

Gupta, S.K. and K.Y. Chen. 1975. Patitioning of trace metals in selective chemical fractions of nearshore sediments. Environ. Lett. 10: 126-158.

Hall, K.J. and K.S. Bindra. 1979. Geochemistry of selected metals in sediments and factors affecting organism concentration. In: Proc. Int. Conf. on Management and Control of Heavy Metals in the Environment, London. CEP Consultants Ltd., Edinburgh, U.K. pp. 337-340.

Hassett, J.P. and M.A. Anderson. 1982. Effects of dissolved organic matter on adsorption of hydrophobic organic compounds by river-and-sewage-borne particles. Water Res. 16: 681-686.

Helsel, D.R. 1986. Estimation of distributional parameters for censored water quality data. In: A.H. El-Shaarawi et al. (Eds.). Statistical Aspects of Water Quality monitoring . Elesvier, Amsterdam.

Hunt, D.T.E. and A.L Wilson. 1986. The Chemical Analysis of Water, General Principles and Techniques, 2nd Edition. The Royal Society of Chemistry, London.

Jaagumagi, R., D. Persaud and T. Lomas. 1989. The In-place Pollutants Program - Vol. V, Part A - A Synthesis of Benthic Invertebrate Studies. Ontario Ministry of the Environment, Toronto.

Jackson, K.S., I.R. Jonasson and G.B. Skippen. 1978 The nature of metal-sediment water interactions in freshwater bodies, with emphasis on the role of organic matter. Earth Science Reviews 14: 97-146. Elesvier Scientific Publishing Co., Amsterdam.

Kadeg, R.D., S.P. Pavlou and A.S. Duxbury. 1986. Elaboration of Sediment Normalization Theory for Nonpolar Hydrophobic Organic Chemicals. Report to Batelle and the U.S. EPA, by Envirosphere Co., 44 p.

Kheborain, C. and C.F. Bauer. 1987. Accuracy of selective extraction procedures for metal speciation in model aquatic sediment. Anal. Chem. 59: 1417-1423.

Krantzberg, G. and P.M. Stokes. 1985. Benthic macroinvertebrates modify copper and zinc partitioning in freshwater - sediment microcosms. Can. J. Fish. Aquat. Sci. 42: 1565-1473.

Landrum, P.F., S.R. Nihart, B.J. Eadie and L.R. Herche. 1987. Reduction in bioavailability of organic contaminants to the amphipod Pontoporeia hoyi by dissolved organic matter of sediment intersitial waters. Environ. Toxicol. Chem. 6: 11-20.

Langston, W.J. 1980. Arsenic in U.K. estuarine sediments and its availability to benthic organisms. J. Mar. Biol. Assoc. U.K. 60: 869-881.

Langston, W.J. 1982. The distribution of mercury in British estuarine sediments and its availability to deposit-feeding bivalves. J. Mar. Biol. Assoc. U.K. 62: 667-684.

Lewis, T.E. and A.W. McIntosh. 1986. Uptake of sediment-bound lead and zinc by the freshwater isopod Asellus communis at three different pH levels. Arch. Environ. Contam. Toxicol., 15: 495-504.

Lomas, T.D. and D. Persaud. 1987. The in-Place Pollutants Program. A Program Overview - Volume 1. Ontario Ministry of the Environment, Toronto. 7 p.

Luoma, S.N., D.J. Cain and C. Johansson. 1985. Temporal fluctuations of silver, copper and zinc in the bivalve Macoma balthica in South San Francisco Bay. Hydrobiologia. 129: 109-120.

Luoma, S.N. 1983 Bioavailability of trace metals to aquatic organisms - a review. Sci. Total Environ. 28: 1-22.

Luoma, S.N. and E.A. Jenne. 1976a. Estimating bioavailability of sediment-bound trace metals and chemical extractants, pp. 343-351. In: Trace Substances in Environmental Health - X. Ed. D.D. Hemphill. University of Missouri, Columbia.

Luoma, S.N. and G.W. Bryan. 1978. Factors contolling the availabiltiy of sediment-bound lead to the estuarine bivalve Scrobicularia plana. J. Mar. Biol. Ass. U.K. 58: 793-802.

Luoma, S.N. and G.W. Bryan. 1979. Trace metal bioavailability: Modelling chemical and biological interactions of sediment-bound zinc, pp. 577-611. In: Chemical Modelling - Speciation, Sorption, Solubility and Kinetics in Aqueous Systems. Ed. E.A. Jenne, Amer. Chem. Soc.

Luoma, S.N. and G.W. Bryan. 1982. A statistical study of environmental factors controlling concentrations of heavy metals in the burrowing bivalve Scrobicularia plana and the polychaete Nereis diversicolor. Estuarine, Costal and Shelf Science 15: 95-108.

Marquenie, J.M. 1985. Bioavailability of micropollutants. Environ. Technol. Ltrs. 6: 351-358.

Marquenie, J.M., W. Chr. de Kock and P.M. Dinnden. 1983. Bioavailability of heavy metals in sediments. In: Proc. Int. Conf. On Heavy Metals in the Environment, Heidelberg. CEP Consultants Ltd., Edinburgh, U.K. pp. 944-947.

McCarthy, J.F. and M.C. Black. 1986. The effect of dissolved organic macromolecules on exposure of aquatic organisms to organic contaminants. CONF-860137-2. NTIS.

McFarland, V.A. 1984. Activity-based evaluation of potential bioaccumulation from sediments, pp. 461-466. In: Dredged Material Disposal, Vol. 1. Eds. R.L. Montgomery and J.W. Leach. American Society of Civil Engineers, New York, N.Y.

Nau-Ritter, G.M. and C.F. Wurster. 1983. Sorption of polychlorinated biphenyls (PCB) to clay particulates and effects of desorption on phytoplankton. Water Res. 17: 383-387.

Neff, J.W., R.S. Foster and J.F. Slowey. 1978. Availabiltiy fo Sediment-absorbed Heavy Metals to Benthos with Particular Emphasis on Deposit-feeding Infauna. U.S. Army COE Waterways Experiment Station, Vicksburg, Mississippi, Technical Report D-78-42. 286p.

Norusis, M.J. 1986. (Ed.) SPSS/PCt for the IBM PC/XT/AT. SPSS Inc., Chicago, Illinois.

Oakley, S.M., P.O. Nelson and K.J. Williamson. 1981. Environ. Sci. Technol. 15: 474.

Oliver, B.G. 1987. Uptake of chlorinated organics from anthropgenically contaminated sediments by oligochaete worms. Can. J. Fish. Aquat. Sci. 41: 878-883.

Pavlou, S.P. and D.P. Weston. 1984. Initial Evaluation of Alternatives for Development of Sediment Related Criteria for Toxic Contaminants Marine Waters (Puget Sound). Phase II: Development and Testing of the Sediment-water Equilibrium Partitioning Approach. Report to the U.S. EPA, by JRB Associates, 89 p.

Pavlou, S.P. and D.P. Weston. 1983. Initial Evaluation of Alternatives for Development of Sediment Related Criteria for Toxic Contaminants in Marine Waters (Puget Sound). Phase I: Development of Conceptual Framework. Report to EPA, JRB Associates.

Persaud, D. and T.D. Lomas. 1987. In-Place Pollutants Program - Volume II. Background and Theoretical Concepts. MOE Report. 34 p.

Persaud, D., T.D. Lomas, A. Hayton. 1987. The In-Place Pollutants Program. Vol. III. Phase I Studies. Ontario Ministry of the Environment, Toronto.

Persaud, D., T.D. Lomas, A. Hayton and S. Petro. 1989. The In-Place Pollutants Program. Vol. IV. Phase I Data Summary. Ontario Ministry of the Environment, Toronto.

Piemontesi, D. and P. Baccini. 1986. Chemical characteristics of dissolved organic matter in interstitial water of lacustrine sediments and its influenece on copper and zinc transport. Environ. Technol. Lett. 7: 577-592.

Prosi, F. 1981. Bioavailability of heavy metals in different freshwater sediments: uptake in macrobenthos and biomobilization. Internat. Conf. Management and Control of Heavy Metals in the Environment. CEP Consultants Ltd., Edinburgh, U.K. pp. 288-291.

Rapin, F., G.P. Nembrimi, U. Forstner and J.I. Garcia. 1983. Heavy metals in marine sediment phases determined by sequential chemical extraction and their interaction with interstitial water. Environ. Technol. Lett. 4: 387-396.

Rapin, F., A. Tessier, P.G.C. Campbell and R. Carignan. 1986. Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure. Environ. Sci. Technol. 20: 836-840.

Reuther, R., R.F. Wright and U. Forstner. 1981. Distribution and chemical forms of heavy metals in sediment cores from two Norwegian lakes affected by acid precipiation. In: Proc. Int. Conf. on Heavy Metals in the Environment, Amsterdam. CEP Consultants Ltd., Edinburgh, U.K. pp. 318-321.

Rezvoi, P.D. and N.S. Yalynskaya. 1960. K metodike opredeleniya biomassy planktona i bentosa. Zool. Zh 39: 1250-1252. (Procedures for determining the biomass of plankton and benthos).

Rodgers, D.W. 1987. Effects of pH and feeding regime on methylmercury accumulation within aquatic microcosms. Environ. Pollut. 45: 261-274.

Rubenstein, N.I. and J.L. Lake. 1986. Contaminant bioavailability from sediments. A research prosposal to the Corps of Engineers, New York District, to develop a screening method for determining contaminant bioavailability from sediments, pp. B219-B223. In: Bioassessment Methodologies for the Regulatory Testing of Freshwater Dredged Material. Eds. T.M. Dillion and A.B. Gibson. M.P. EL-86-6.

Saffer, M. 1985. (Ed.). SAS Procedures Guide for Personal Computers, Version 6. SAS Institute Inc., Cary, N.C.

Sakata,M. 1985. Diagenetic remobilization of manganese, iron, copper and lead in anoxic sediment of a freshwater pond. Water Res. 19: 1033-1038.

Shea, D. 1988. Developing national sediment quality criteria. Environmental Science and Technology 22: 1256-1261.

Sokal, R.R. and F.J. Rohlf. 1981. Biometry. The Principles and Practice of Statistics in Biological Research. W.H. Freeman and Co.

Steel, R.G.D. and J.H. Torrie. 1960. Principles and Procedures of Statistics with Special Reference to the Biological Sciences. McGraw-Hill, New York.

Tessier, A., P.C.C. Campbell, J.G.C. Auclair and M. Bisson. 1984. Relationships between the partitioning of trace metals in sediments and their accumulation in the tissues of the freshwater mollusc Elliptio complanata in a mining area. Can. J. Fish. Aquat. Sci. 41: 1463-1472.

Thomson, E.A., S.N. Luoma, D.J. Cain and C. Johansson. 1980. The effect of sample storage on the extraction of Cu, Zn, Fe, Mn, and organic material from oxidized estuarine sediments. Water Air Soil Pollut. 14: 215-223.

Winberg, G.G. 1971. Methods for Estimation of Production of Aquatic Animals. Academic Press. pp. 175.